(25) J. Mazur and D. McIntyre, *Macromolecules*, 8, 464 (1975).

(26) Technical difficulties would be encountered if the $\lim_{k\to 0}$ were taken before the evaluation of integrals. To overcome these problems and enable the analytical evaluation of these integrals, recourse is made to the theory of generalized functions.[27] The integrals are unchanged if a factor $\lim_{k\to 0}$ $\exp(-\epsilon x)$ is inserted in them. Then, the orders of $\lim_{k\to 0}$ and $\lim_{\epsilon\to 0}$ may safely be interchanged, and the ϵ limit can be evaluated *after* all integrals have been performed.

(27) P. Dennery and A. Krzywicki, "Mathematics for Physicists", Harper and Row, New York, N.Y., 1967, p 225 ff.

A Study of Equilibrium Melting of Polyethylene

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ABSTRACT: The equilibrium melting of polyethylene is discussed based on new and literature data. Melting temperatures, superheating effects, and heats of fusion are determined on well-crystallized chain folded and extended chain crystals as well as fully extended chain crystals produced by etching. Extrapolation procedures of melting temperatures are critically evaluated. The superheating is shown to be mainly due to effects of the amorphous areas on the crystals, but some superheating remains for sufficiently large crystals after removal of the amorphous material. The heat of fusion is shown to have a surprising temperature dependence which gives a reason for errors in melting temperature extrapolations. The experimental data on volume change on fusion are summarized. The entropy of fusion is discussed in terms of the conformational change which, however, is not approximated by the constant volume entropy of fusion. The following best values have been derived: melting temperature 414.6 ± 0.5 K, crystal volume 1.0338 m^3/Mg, amorphous volume 1.2765 m^3/Mg, heat of fusion 4.1 ± 0.2 kJ/mol of CH_2, and conformational melt entropy 7.8 ± 1.0 J/K/mol of CH_2.

The equilibrium properties of crystals of flexible, linear macromolecules are difficult to obtain experimentally. On crystallization from the melt or from solution, already polymerized molecules go first to a chain-folded macroconformation.[1] This leads, at least initially, to grossly metastable crystals. For many years no conditions were known to produce anything but these metastable chain folded crystals. Their analysis furthered the belief that: "Crystallizing high polymers have no sharp melting point".[2] A major effort was, for this reason, undertaken to develop extrapolation procedures to guess at the equilibrium properties. In the meantime, annealing of metastable crystals, as well as crystallization during polymerization, have led to a number of crystals of linear macromolecules which closely approximate equilibrium crystals.[1] In practice this means that crystals of high perfection of sizes above 1 μm in all crystallographic directions have been grown. It is thus possible to have an experimental check on the quality of these extrapolations.

In this paper we are concerned with polyethylene. Experimental data on crystals close to equilibrium became available with the first crystallization from the melt under hydrostatic pressures above 300 MN/m^2.[3] In the present research new data on heats of fusion, melting temperatures, and superheating behavior of a series of more or less extended chain crystals have been derived. They will be combined with older data from our laboratory and with literature data to enable a critical comparison with extrapolated equilibrium properties. Of main interest are data on the equilibrium melting temperature, the heat of fusion, the volume change on fusion, and the entropy of fusion. It will be shown that presently extrapolations and experiments agree within the error limits of the methods.

The first step in the analysis is the proof that the above statement about the diffuse melting of macromolecules is true only for metastable crystals. Equilibrium crystals of flexible linear macromolecules melt as sharply as small molecules. Figure 1 illustrates such proof for the melting of high molecular weight polyethylene crystallized under elevated pressure (sample PM, below). About 80% of the whole sample can be seen to melt within 1.6 K, and the highest melting crystals are largest in number and give a sharp melting temperature of 414.6 K.[4] Since the largest crystals in this sample were 10 μm or more in all dimensions, had a density which agreed with the x-ray density, and contained no fractions below 10^5 molecular weight, they must melt with a typical experimental error of ±0.5 K at the equilibrium melting temperature.[54] This conclusion, which was reached almost 15 years ago and was frequently criticized,[5] will be shown to be supported by the new experiments and also by properly adjusted extrapolations.

A major problem in experimentation with extended chain crystals is their tendency to superheat before melting. Superheating of the extended chain crystals will be shown to result from two sources: inherently slow melting of large macromolecular crystals and restriction of melting by remaining loops and tie molecules.

Experimental Section

Materials. Linear polyethylene of number average molecular weight 8530 and weight average 153 000 was used. A molecular weight distribution curve of this polymer has been shown in ref 6. A high molecular weight sample, referred to as polymethylene, was made from diazomethane with an estimated molecular weight of 1.4×10^7. The lowest fraction in this polymer, detectable by gel permeation, was above 10^5 in molecular weight.

The crystallization conditions were guided by prior experience. The polymethylene was crystallized at 500 K and 482 MN/m^2 pressure for 20 h and then slowly cooled at a rate of 1.6 K/h to room temperature for pressure release. This sample is called PM. Its 296 K density is 0.997 Mg/m^3, and its dilatometric melting point on slow heating was determined earlier as 414.6 K (see Figure 1; sample 31 in ref 4). Crystallizing this polymer without the aid of elevated pressure from the melt by quick quenching led to a crystallinity of only 0.37 and a DTA melting peak temperature of 404.9 K.

The polyethylene was crystallized both under elevated pressure and by long-term crystallization at atmospheric pressure. The pressure crystallization was carried out at 509 K and 507 MN/m^2 for 24 h and was followed by fast cooling to room temperature. The 296 K density of this sample was 0.982 Mg/m^3, considerably less than the best samples crystallized from the same polymer at elevated pressure. This sample will be called P509. The atmospheric pressure sample was crystallized isothermally for 21 days at 402.2 K before quick cooling to keep the segregated, low molecular weight polymer poorly crystallized. This sample will be called P402. Its 296 K density is 0.977

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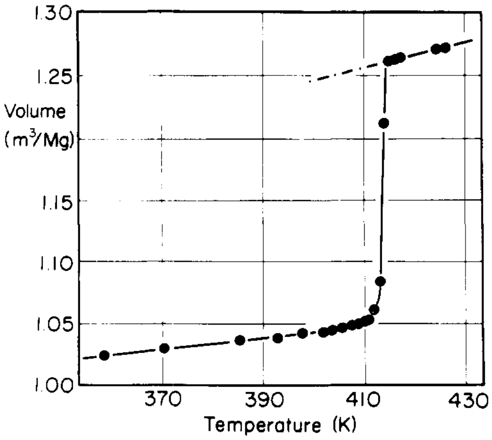

Figure 1. Change in specific volume of high molecular weight, extended chain crystals of polyethylene on melting; sample PM. Data from ref 4.

Mg/m^3 (sample C129 in ref 7). From this sample the low molecular weight portion was extracted by careful dissolution in p-xylene. This changed the viscosity molecular weight from 68 000 to 87 380 for the crystals. The extracted portion had a viscosity average molecular weight of 44 400 and amounted to 52% of the whole sample. The extracted P402 had a 296 K density of 0.983 Mg/m^3. Crystallizing the polyethylene by quick quenching, as the polymethylene above, resulted in a crystallinity of 0.55 with a DTA melting peak temperature of 401.5 K.

Differential Thermal Analysis. For determination of the time dependence of melting, a du Pont 900 thermal analyzer was used with capillary glass sample holders (2 mm outside diameter). The DTA furnace consisted of a silver block (2.2 cm diameter) with a 150 W central cartridge heater (0.95 cm diameter). The sample was placed at the bottom of the glass capillary and held in place with a fixed, centered thermocouple. Calibration was done with indium, a metal which was shown not to superheat at such rates.[8] Previous superheating experiments involved sandwiching the sample between layers of alumina, which is also used as the reference material.[9] A comparison showed that both methods give similar results, but the simpler procedure of placing the sample at the bottom of the capillary is more reproducible and quicker to set up. For small weights (0.05 to 1.0 mg) the onset of melting, which is obtained by extrapolating the low temperature side of the melting peak back to the baseline, and the peak temperature suffer little, if any, instrument lag up to 100 K/min. The melt end, however, lags at 80 K/min even for the smallest weight by as much as 7 K, this lag increases for 1 mg samples to about 11 K. The method used for all superheating studies is to quote peak temperatures and to change sample mass with increasing heating rate so that the peak area matches that of indium of less than 0.5 mg, molten at 10 K/min.

Differential Scanning Calorimetry. All heats of fusion were determined by a calculator connected Perkin-Elmer DSC-2.[10] Measurements were made at a heating rate of 10 K/min on samples of one to several milligram size. The amplitudes were sampled every 0.6 s (10 000 subdivisions for full scale deflections, typical melting peaks of 5000–8000 divisions above the baseline). The data were permanently stored on punched paper tape. The tapes are then read by a tape reader (Hewlett Packard 2748 B) and evaluated with help of a programmable calculator (Hewlett Packard 8621 B). The baseline is established by interpolation between crystal and melt baseline according to the total fraction molten. Heats of fusion can be obtained with this equipment to 1–2% accuracy for reproducible and sharply melting materials.

Etching. Etching techniques for polyethylene are well known.[1] To establish intermediate states, a 90% fuming nitric acid at 333 K was chosen as the oxidation condition.[11] Cubes of 2–3 mm size of sample were sealed in glass tubes with excess acid (100 mL acid/g of polymer). The time of etching was varied between 0.5 and 100 h. After etching, the crystals were washed in distilled water, followed by acetone (24 h). For separation and analysis of the morphology, ultrasonic dispersion was used. Details about the observed morphology are published elsewhere.[12]

Molecular Weight. Molecular weights after etching were determined by dilution viscometry in p-xylene with n-phenyl-2-naphthylamine as antioxidant. After a long etching time, the viscosity average molecular weight was taken to agree with the thickness average of the crystal lamellae. The proof of this assumption was presented earlier.[11,13] The molecular weights after 100 h of etching for P402, P509, and PM were 7230, 12 800, and 84 200 or 515.3, 912.3, and 6001.4 CH$_2$ groups, respectively. These values are in accord with crystal size distribution estimates given earlier.[6]

Results and Discussion

(A) The Equilibrium Melting Temperature. The melting temperature of sample PM is shown in Figure 1. Slow dilatometry was necessary for its determination because of superheating (see below). Thermal analysis could not get new precise melting data on PM and the two other well-crystallized samples since the increase in melting temperature with heating rate is nonlinear, showing an almost vertical tangent at zero heating rate (see Figure 6, below). This changes after 100 h of etching. The melting temperatures are now determined on crystals of fully extended chain macroconformation. The melting data are listed in Table I (samples e). Also listed in Table I are literature data for high purity paraffins up to 140 carbon atoms (samples a and c). Furthermore, melting temperatures of solution grown polyethylene crystals of low fold length after etching and conversion to paraffins are also shown (samples b). It was documented on these samples that for paraffins of length of the order of magnitude of 10 nm a somewhat larger melting temperature results if the etched samples with carboxyl chain ends are measured directly.[13] These increases in melting temperature go to zero as the chain length increases. Finally, Table I also contains data on three samples derived from similar etching experiments on crystals of high perfection (samples d).[11] Table I represents thus the present best set of experimental melting points of C_xH_{2x+1} molecules with melting points above 375 K. Lower paraffin data (down to $C_{11}H_{24}$) are well known from the compilation of Flory and Vrij.[14]

Extrapolations of melting temperatures of paraffins to longer chain length were done repeatedly since 1884,[16] with results ranging from 385 to 420 K. Most of the earlier extrapolations were based on the assumption of a linear increase with chain length of the heat of fusion ΔH and the entropy of fusion ΔS. A detailed discussion of the melting and evaporation of long chain compounds as a function of chain length was given by Huggins.[17] As long as linearity is preserved, the melting temperature can be expressed as

$$T_m = \frac{\Delta H}{\Delta S} = T_m{}^0 \frac{(a + x)}{(b + x)} \tag{1}$$

The fitting of the most comprehensive set of melting temperatures of paraffins which crystallize in the orthorhombic polyethylene-like crystal structure was done by Broadhurst[18] on 14 paraffins ($C_{44}H_{90}$ to $C_{100}H_{202}$). The result was

$$T_m = 414.3 \frac{x - 1.5}{x + 5.0} \tag{2}$$

Figure 2 shows this function as the drawn out curve. It fits the data of Table I with a practically random average error of +0.004 K and a standard deviation of ±0.9 K (see also Figure 8, curve 1). The original set of paraffins is represented by eq 2 with a standard deviation of ±0.3 K. One would consider this agreement within present error limits.

The functional form of eq 1 is, however, not in agreement with the lattice model of melting of linear macromolecules. A logarithmic term in x must be included in the entropy of fusion in addition to the linear increase given by eq 1.[14] Such a logarithmic term was first suggested by Huggins in 1939 on assessing the molecular length effect on entropy of linear macromolecules able to translate and rotate as a whole.[17] One can model the melting of the paraffins occurring in two stages.[14] First, one can assume chains of paraffins to melt without disconnecting at the CH$_3$ ends of adjoining molecules

Table I
Melting Temperatures of Fully Extended Chain Crystals C_xH_{2x+2} in K

x	Ref	T_m	Eq 2	Δ	Eq 6	Δ
64	*a*	375.3	375.3	+0.03	375.5	−0.2
66	*a*	376.8	376.4	+0.4	376.6	+0.2
67	*a*	377.3	376.9	+0.4	377.2	+0.1
70	*a*	378.5	378.4	+0.1	378.7	−0.2
75.4	*b*	380.8	380.8	−0.06	381.2	−0.4
82	*a*	383.5	383.3	+0.2	383.9	−0.4
84.8	*b*	383.4	384.3	−0.9	384.9	−1.5
94	*a*	387.0	387.1	−0.1	387.9	−0.9
100	*a*	388.4	388.7	−0.3	389.5	−1.1
120	*c*	392.2	392.8	−0.6	393.9	−1.7
140	*c*	394.2	395.7	−1.5	397.2	−3.0
335.0	*d*	408.1	406.4	+1.7	409.3	−1.2
377.8	*d*	409.3	407.3	+1.9	410.3	−1.0
515.3	*e*	409.2	409.1	+0.1	412.6	−3.4
912.3	*e*	411.2	411.4	−0.2	415.5	−4.3
3863.2	*d*	412.6	413.6	−1.0	418.6	−6.1
6001.4	*e*	413.6	413.9	−0.3	419.0	−5.4
(∞	*f*	414.6	414.3	+0.3	419.7	−5.4)

[a] Data on paraffins as collected in ref 14. [b] New paraffin data by etching of solution grown polyethylene and conversion of the dicarboxylic acids to iodides or paraffins (ref 13). [c] New paraffin data described in ref 15. [d] Etched single crystals of crystallinity close to 100%; x calculated after etching from the weight average molecular weight (ref 11). [e] This research. [f] Maximum melting temperature without etching, melt end; largest crystal in distribution corresponds to x = 78 000, smallest molecules x = 7000 (ref 4).

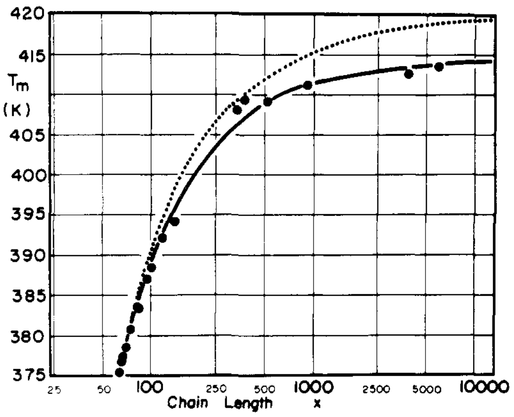

Figure 2. Melting temperature of C_xH_{2x+2} as a function of chain length x. For data see Table II. Drawn out line calculated from eq 2 and dotted line calculated from eq 5.

from adjacent crystal layers. This process is analogous to polyethylene melting. Second, the molecules are separated, which takes at each junction point a free enthalpy of Δg_e and an entropy term $RT \ln x$. The entropy term accounts for the random placements of the first segment of each new molecule and can also be interpreted as the entropy of unpairing the molecular ends. Overall, the free enthalpy of melting per mole of molecules x units in length is thus

$$\Delta G = x\Delta g_f + \Delta g_e - RT \ln x \qquad (3)$$

From eq 3 it can be seen that a melting point equation should have the form[55]

$$T_m = T_m{}^0 \frac{a + x}{b + x + c \ln x} \qquad (4)$$

where a is $\Delta h_e/\Delta h_f$, b is $\Delta s_e/\Delta s_f$, and c is $R/\Delta s_f$. Assuming the ratios a to c to be temperature independent and setting $R/\Delta s_f \approx 1.0$, one can derive the following least-squares expression for the melting temperature[19]

$$T_m = 419.6 \frac{x - 3.48}{x + \ln x - 0.45} \qquad (5)$$

For the derivation of eq 5 the expanded data set as collected by Flory and Vrij[14] was used. It includes melting data of 33 paraffins from $C_{11}H_{24}$ to $C_{100}H_{202}$. The new equation fits this set of melting temperatures with a standard deviation of ±0.4 K. Without refitting the parameters of eq 2 to the larger data base, it also gives a standard deviation of ±0.4 K and an average deviation of −0.08 K. The new equation shows, however, a $T_m{}^0$ which is 5.3 K higher, a deviation beyond the experimental uncertainty (see also Figure 8, curve 2).

Beyond the assumption of constant parameters for all temperatures, Broadhurst[20] derived new melting point equations with estimated temperature dependencies. The latest form of this equation included several changes in addition to the least-squares fitting of three parameters by Broadhurst[21]

$$T_m = 419.7 \frac{x - 0.542}{x + 0.46[7.667 + 1.987 \ln x + (5.6/x) - (0.25x - 7.0)(1 - T_m/419.7)]} \qquad (6)$$

The standard deviation of this equation for the set of paraffin melting points it was derived from[20] is ±0.6 K with an average deviation of 0.11 K, hardly an improvement over the simple eq 2 and 5. The value of $T_m{}^0$ is again higher than can be supported by experiment (see also Figure 8, curve 3).

Table I shows the fit of eq 2 and eq 6 to the higher paraffin and polyethylene data derived here. Equation 2 represents these data well with a practically random average error of only +0.004 K and a standard deviation of ±0.9 K, while eq 6 shows a positive average error of 1.79 K (which systematically increases for larger molecules) and a larger standard deviation of ±1.9 K. To resolve the question why equations which have a more correct form give poorer fit of the experimental data, we will need to discuss the temperature dependence of Δh_f below. First we would like to look at some alternate extrapolations.

An alternate way to evaluate the equilibrium melting temperature of large crystals is to measure the melting temperature of well-defined small crystals and extrapolate to infinite size using the Thomson-Gibbs equation. For lamellar crystals this extrapolation is particularly simple, since only the large lamellar surface contributes significantly to the free enthalpy.

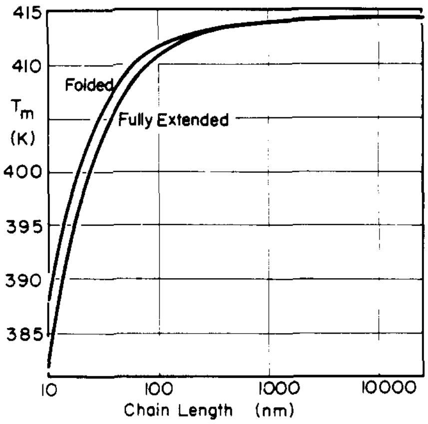

Figure 3. Melting temperatures of lamellae of polyethylene as a function of lamellar thickness l. Upper curve, folded chain lamellae of high molecular weight, calculated from eq 7 with $2\gamma/\Delta h_f = 0.627$. Lower curve, fully extended chain lamellae of paraffins and polyethylene of molecular weight $110.2l$, calculated from eq 2, l in nm ($l = 0.1273x$).

$$T_m = T_m^0\left(1 - \frac{2\gamma}{l\Delta h_f'}\right) \qquad (7)$$

where γ is the lamellar surface free energy, l is the lamellar thickness, and $\Delta h_f'$ is the heat of fusion per unit volume. Equation 7 has the advantage over paraffin melting temperature extrapolations that the temperature range for extrapolation to large crystals is smaller so that the change of $\gamma/\Delta h_f'$ with temperature is not a large problem. In addition, part of the temperature effect may cancel within the ratio. Figure 3 shows a typical comparison of the paraffin extrapolation and the small crystal extrapolation. Paraffin data are most plentiful between 1.4 to 15 nm, while typical lamellar crystals range from 10 to 100 nm.

The major difficulty in using eq 7 is the instability of small crystals. Thin lamellae will anneal on heating to the melting temperature and show experimentally only the higher melting temperature of the perfected crystal.[1] Large lamellae, on the other hand, may show superheating. Various methods have been developed to hinder annealing. The two major methods are fast melting, so that not enough time remains for annealing[9] and cross-linking in the amorphous region, so that the chains are hindered on annealing.[22,23] Figure 4 shows data on solution and melt crystallized polyethylenes selected so that the melting conditions excluded annealing or superheating. The straight line follows the equation

$$T_m = 414.2(1 - \frac{0.627}{l}) \pm 0.8\text{ K} \qquad (8)$$

where l is given in nm. Remaining possible systematic errors in eq 8 may involve inhomogeneity of the samples (low molecular weight and copolymer components may reduce the melting temperature due to solvent effects), uncertainty in lamellar thickness measurement (especially for melt crystallized samples and lamellae with inclined chains), variation in $2\gamma/\Delta h_f'$ with l and T, and finally changes in lamellar perfection and extension. On the strength of Figure 4 one would say, however, that these effects are small, cancel, or are largely proportional to $1/l$. With the heat of fusion to be derived below (4.11 kJ/mol of CH_2) one can calculate the surface free energy of polyethylene lamellae γ to be 0.0918 J/m^2 (91.8 erg/cm^2).

Several other extrapolation methods have been developed which lack, however, a full theoretical proof. Since lamellar crystals often have a thickness similar to those of primary nuclei, it was suggested that a plot of T_m vs. T_c, the crystallization temperature, could give an estimate of T_m^0.[24]

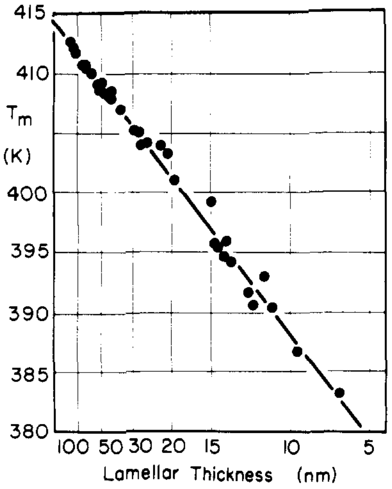

Figure 4. Melting temperatures of polyethylene lamellar crystals as a function of reciprocal lamellar length as suggested by eq 7. Data collected by Illers and Hendus.[23]

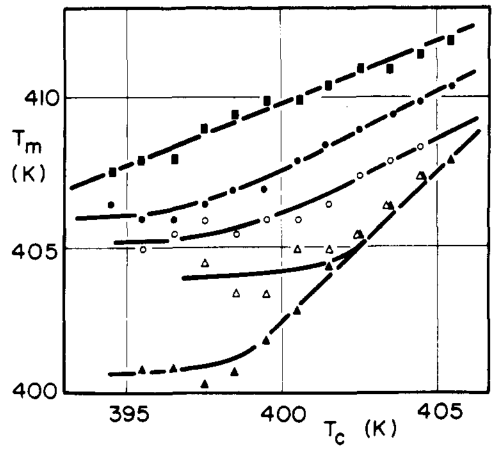

Figure 5. Melting temperatures of polyethylene at various temperatures. Melt crystallization of a broad molecular weight distribution polyethylene (M_w = 80 000). The crystallization and melting were done in a scanning calorimeter, seeded with extended chain crystals. The crystallization times varied between less than 0.5 min to over 6000 h. The heating rate after crystallization was 5 K/min. The open triangles and circles refer to the temperatures of beginning of melting and the melting peak of the first grown crystals (less than 0.01 total crystallinity). The filled triangles, circles, and squares refer to the temperatures of beginning of melting, the melting peak, and the last trace of melting after completion of crystallization.[25]

$$T_m = [T_m^0(2\beta - 1) + T_c]/(2\beta) \qquad (9)$$

In this equation β is the fold length in multiples of the primary homogeneous nucleus fold length. As long as β stays constant for various crystallization temperatures, eq 9 describes a family of straight lines for different β's which all intersect when $T_m = T_c = T_m^0$. Figure 5 shows typical polyethylene data on melt crystallized polyethylene. The maximum melting temperature after completion of crystallization and perfection (solid squares) gives a good straight line which yields with eq 9 a T_m^0 of 416.6 K with a β of 1.24. Using only the first seven points leads to a T_m^0 of 418.9 K and a β of 1.08. The melt begins and peaks all show signs of annealing on heating for low crystallization temperatures (horizontal portions of the curves). The later portions of the melting peak curves extrapolate to 413 K (open circles) and 416 K (filled circles). The beginning of melt (triangles) has a steeper slope than 45° and cannot be used to evaluate T_m^0. Similar variations in β had been observed earlier by Weeks.[26] Adding to these difficulties

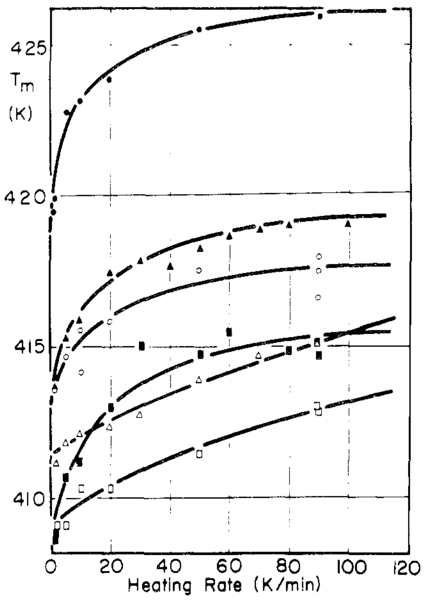

Figure 6. Melting peak temperatures of polyethylene crystals before and after etching. Before etching, filled symbols; after etching for 100 h, open symbols. Circles, sample PM; triangles, sample P509; squares, sample P402.

are the systematic errors mentioned on discussion of eq 8. Other methods of estimation of the equilibrium melting temperature make use of glass transition–melting transition correlations[27] (403 K), derived empirical group contributions[28] (414 K), or entropy estimates.[29] All these extrapolations add little to the present discussion because of the uncertain theoretical basis of the methods.

(B) Superheating. The research into superheating began when it became advantageous to heat metastable crystals fast to avoid reorganization before melting. The first detailed polyethylene data were shown in ref 9. Initially it was thought only the size of extended chain crystals in relation to the melting rate was the cause of superheating. As more experimental material became available, it became clear that hindering of macroconformations after melting may also cause superheating. This explanation was first proposed by Zachmann.[30] The discovery of the special properties of polyethylene crystallized in the presence of extensional flow[31] dramatized the superheating due to hindering of macroconformations by providing samples of poor crystallization which retained birefringence up to 460 K.[32] Recently, we could demonstrate[33] that both order in the amorphous phase and remaining crystals are necessary for this high-temperature birefringence. As soon as tie molecules between the crystals are cut by etching, the high melting temperature disappears and instead values of about 405 K are found (in accord with crystal size estimates). Efforts to derive equilibrium melting temperatures from maximum melting temperatures of oriented semicrystalline samples[34] are thus most likely to give erroneously high values. It was shown some time ago[11] that etching extended chain crystals reduces their superheating substantially. Figure 6 shows the results for the three newly analyzed samples. Before etching, the melting peak temperature rises rapidly on changing the heating rate from 1 to 20 K/min and more slowly at higher heating rates. For samples PM and P509 (circles and triangles), the increase is so rapid that the tangent at zero heating rate is almost 90° so that an extrapolation to zero heating rate is hardly possible. After etching, only the PM sample shows some definite remaining curvature; P509 and P402 show almost linear increases in melting peak temperature with heating rate which is easy to extrapolate to zero heating rate (values listed in Table I). At higher heating rates there is a definite remaining superheating, not caused by effects of the amorphous areas on the crystal. Slow melting of polyethylene crystals must be the cause of superheating in these experiments. Quantitative analysis of the melting rates must await the preparation of separate single crystal preparations and measurement of the size as a function of time through optical microscopy. Initial efforts in this direction are underway in our laboratory.

Table II
Heats of Fusion in kJ/mol at T_m

Sample	Melting temp, K[c]	Δh_f	Density,[d] Mg/m^3
PM (unetched)	423.9	4.005	0.995
PM (etched[a])	415.6	4.166	1.00
P509 (unetched)	415.9	3.425	0.981
P509 (etched[a])	412.2	3.701	1.00
P409(unetched, unextracted)	411.7	3.257	0.997
P402 (etched,[a] unextracted[b])	411.2	3.618	1.00
P402 (unetched, extracted)	411.4	3.443	0.983
P402 (etched,[a] extracted[b])	410.3	3.681	1.01

[a] 100 h of etching. [b] Crystals grown on cooling of the sample were extracted (see above). [c] Measured at 10 K/min heating rate by DTA. [d] At 296 K measured with a density gradient column.

(C) Heat of Fusion. The equilibrium heat of fusion of polyethylene is a much less controversial topic. The DSC results derived here are shown in Table II. Etched, as well as unetched, samples are listed together with the 10 K/min DTA melting peak temperatures and with densities. The PM sample is close enough to perfect crystallization to take its heat of fusion as the equilibrium value. Earlier measurements on a lower molecular weight extended chain sample of similar density (0.997 Mg/m^3) showed a similar heat of fusion (4.015 kJ/mol).[35] A collection of heats of fusion of many semicrystalline samples by Hendus and Illers[36] led to the following linear equation for heats of fusion of polyethylene as a function of specific volume v (in m^3/Mg) at room temperature

$$\Delta h_f = 4.109 - 25.65(v - 1.00) \quad \text{(in kJ/mol of CH}_2\text{)} \qquad (10)$$

Adding the new samples to the large data base of eq 10 would not change the heat of fusion of an equilibrium crystal. The best experimental value is thus 4.1 kJ/mol of CH_2. The etched samples except for PM show clearly a 10% too low heat of fusion for the measured density. The origin of this lower heat of fusion is not known. If we assume it to be proportional to the surface area, its effect would be 1% for PM, or less than the experimental error.

Extrapolation of heats of fusion from semicrystalline polyethylenes was done not only using density as variable but also chain length. As one would expect, both surface and internal perfection affect the heats of fusion. The slope in eq 10 includes thus not only changes due to crystal perfection, although this is the largest part, but contains also smaller amounts of heat of fusion changes due to changes in surface area. Trying to separate these effects is at the present limit of heat of fusion and density determination. References 37–39 contain more detailed discussions. All are, however, in reasonable agreement with a 4.1 kJ/mol of CH_2 heat of fusion. The total remaining systematic error is probably less than ±0.2 kJ/mol of CH_2 (see also Figure 7 in the temperature range 350–450 K).

Further support of the heat of fusion data comes from diluent effect studies. Despite the need to apply equilibrium

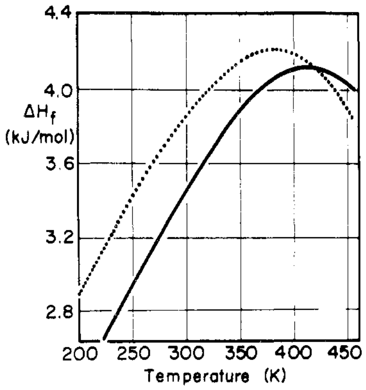

Figure 7. Heat of fusion of polyethylene as a function of temperature. Drawn-out curve as derived from paraffin data in eq 12. Dotted curve from polyethylene heats of fusion at the melting temperature and heat capacities (ref 47).

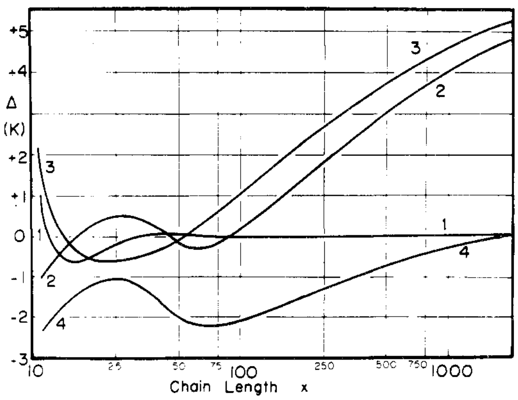

Figure 8. Deviations of melting temperatures calculated with the various equations from the experimental data. A smoothed curve has been drawn from plots of all points. The actual points scatter by about 0.5 to 2 K about the drawn curves: curve 1, eq 2; curve 2, eq 5; curve 3, eq 6; curve 4, eq 3 with data of eq 12 and 13.

thermodynamics to the clearly nonequilibrium melting experiments an average of six different analyses[40–42] leads to 4.0 kJ/mol of CH_2.

Extrapolations of heats of fusion of paraffins to polyethylene have also been attempted. The data base consists in this case of 26 paraffins from the group C_6H_{14} to $C_{48}H_{98}$.[43,44] The first observation in these studies was that the heat capacities of liquid paraffins and polyethylenes are identical.[45] The most recent set of measurements[46] on polyethylene covered liquid polyethylene from 413 to 633 K. This heat capacity equation fits also all paraffin data with an error of less than ±1.5% down to 230 K.

$$C_{p_a} = 20.0 + 3.368 \times 10^{-2}T + 9.91 \times 10^{-6}T^2 \quad (C_{p_a} \text{ in J/K/mol of CH}_2) \tag{11}$$

Referred to a common temperature above the melting temperature, enthalpies per mole of CH_2 of all liquid alkanes and of polyethylene are thus identical. With the established liquid enthalpies, it is now possible to integrate experimental data numerically to the lower temperatures of the crystalline state and establish enthalpies, entropies, and free enthalpies as a function of temperature and chain length relative to a given reference in the molten state. Changes in these quantities on fusion are independent of the reference temperature. For use in eq 3 the following quantities were derived[44]

$$\Delta g_f = 1.308 + 1.263 \times 10^{-2}T - 5.96 \times 10^{-5}T^2 + 5 \times 10^{-8}T^3 \tag{12}$$

$$\Delta g_e = -0.520 - 7.74 \times 10^{-2}T + 1.09 \times 10^{-4}T^2 \tag{13}$$

For large x eq 3 goes to zero for the equilibrium melting temperature. With eq 12, a melting temperature of 414.8 K results, in good accord with the experimental value of Figure 1. Furthermore, the heat of fusion can be determined from eq 3 and 12 by finding $-T^2\partial(\Delta G/T)/\partial T$ at the melting temperature. At 414.6 K, 4.14 kJ/mol of CH_2 results in good agreement with the experimental data and crystallinity extrapolation.

Since we now have an empirical expression for the temperature dependence of all thermodynamic parameters, it is possible to attempt to solve the problem of the melting temperature extrapolations of eq 5 and 6. Figure 7 shows the heat of fusion as a function of temperature as derived from eq 12. Also shown in Figure 7 is the heat of fusion calculated from the experimental heat of fusion and the heat capacity difference between amorphous and completely crystalline polyethylene.[47] The heat of fusion shows a definite maximum at about 380 K. None of the extrapolation attempts has taken this maximum into account. Using eq 12 and 13 to derive a melting temperature equation like eq 4 leads to a complicated equation with up to cubic terms in T_m in the numerator and up to quadratic terms in T_m in the denominator. Solving by iteration is, however, easy. Only two or three iterations give constant values for T_m. The most important result of this calculation is an almost complete disappearance of the positive deviation trend at high temperatures. Figure 8 shows the trends of the differences between calculated and measured values for the whole range of experimental data for the various equations. The systematic errors are obvious. Although eq 12 and 13 lead for small x to temperatures displaced by 1 to 2 K to lower temperatures, it can be seen that much smaller changes than the experimental uncertainty in the heats of fusion are necessary to fit the data. The systematic error in eq 5 and 6 is thus caused by an unexpected temperature trend of the thermodynamic parameters. Similarly, the good fit of eq 2 can be linked to accidental cancellation of errors.[56]

(D) Volume Change on Fusion. Rather than measuring the volume change on fusion directly from dilatometric experiments as shown in Figure 1, it is more accurate to take the difference of liquid polymer specific volume measured by dilatometry and x-ray lattice parameters. The liquid polymer specific volume is largely unaffected by branching or copolymerization with chemically similar comonomer. Although measurements are only made at high temperature, it was found that these can easily be extrapolated linearly to temperatures as low as 270 K.[48] Crystalline volumes, however, depend on crystal imperfections. Using liquid data as derived and compared to other literature data by Richardson et al.[49] and crystal data by Davis et al.[50] leads to the following equation for the volume change on melting as a function of temperature.

$$\Delta v_f = -0.0564 + 9.401 \times 10^{-4}T - 5.27 \times 10^{-7}T^2 \quad (T \text{ in K}, \Delta v_f \text{ in m}^3\text{/Mg}) \tag{14}$$

The equation should be useful between 270 and 430 K. For small fold lengths, corrections have to be applied.[50] At 414.6 K, eq 14 leads to a volume change of 0.243 m^3/Mg. Crystallinities calculated with the help of eq 14 compare well with crystallinities computed from the heats of fusion.

(E) Entropy of Fusion. With the just established heat of fusion and the equilibrium melting temperature, the entropy of fusion is 9.91 J/K/mol of CH_2.

Some effort has been made to interpret this entropy in terms of its separate contributions. Of particular interest is the conformational entropy gain on fusion ΔS_{conf}. Usually one makes the assumption that the conformational entropy of the molten molecules is a close approximation to ΔS_{conf}. Furthermore, one assumes that the isolated, unperturbed chain

Table III
Conformational Entropies of Polyethylene Calculated for the Isolated Chain[a]

Approximation	ΔS_{conf}, J/K/mol of CH_2
(a) 3 rot. isomers of equal energy (R ln 3)	9.12
(b) Trans conformation more stable by 3.35 kJ/mol[b]	8.16
(c) Trans conformation more stable by 2.26 kJ/mol[b]	8.70
(d) 3 rot. isomers of equal energy, but gauche(+)-gauche(−) sequences forbidden[a]	7.53
(e) Trans conformation more stable by 3.35 kJ/mol, gauche(+)-gauche(−) sequences forbidden[a]	6.65
(f) Trans conformation more stable by 2.26 kJ/mol, gauche(+)-gauche(−) sequences forbidden[a]	7.03
(g) Exact lattice model (diamond lattice), short chains (6–18 °C) extrapolated to ∞, trans conformation more stable by 3.35 kJ/mol[a]	6.61
(h) Rot. isomeric states model (150C), trans. conformation more stable by 2.09 kJ/mol, gauche(+)-gauche(−) hindered by 12.55 kJ/mol[c]	7.41

[a] Following the tabulation by R. P. Smith, *J. Polym. Sci., Part A-2,* **4,** 869 (1966). [b] H. N. V. Temperley, *J. Res. Natl. Bur. Stand.,* **56,** 55 (1956). [c] A. E. Tonelli, *J. Chem. Phys.,* **52,** 4749 (1970).

has close to the same conformational entropy as the chain in the melt. Various calculations of this conformational entropy of the isolated chain are listed in Table III. The simplest estimate (a) is based on three rotational isomers of equal energy and does not take into account any steric hindrance from next nearest neighbors or atoms further along the chain. This entropy should be an upper limit of ΔS_{conf}. Introducing various hindering potentials in the gauche conformation to account for next nearest neighbor interaction along the chain leads to a small, temperature-dependent reduction in conformational entropy (b and c). A larger reduction is caused by inclusion of the so-called pentane interference in the calculation which arises when a gauche(+) conformation is followed by a gauche(−) conformation or vice versa. The entries d to f in Table III illustrate the influence of the pentane interference. Interference due to segments even further removed along the chain can only be taken into account in an exact lattice treatment. Entry g in Table III shows such a calculation. It yields an almost insignificant further reduction in the conformational entropy. These rigid lattice calculations should give the lower limit of conformational entropy. A more realistic approach is to account for the pentane type interference by repulsion potential instead of complete rejection. This has been done using the rotational isomeric states model and leads to perhaps the best estimate (h). One should remember that intermolecular effects are still completely ignored in these calculations. The conformational entropy thus calculated is about 75% of the total entropy of fusion.

Efforts to calculate the conformational entropy change from experimental data were made by assuming the constant volume entropy of fusion ΔS_V to be equal to ΔS_{conf}.[40] For the calculation, one makes use of the thermodynamic relations

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V = -\frac{(\partial V/\partial T)_P}{(\partial V/\partial P)_T} = \frac{\alpha}{\beta} \qquad (15)$$

$$\Delta S_V = \Delta S_f - (\partial S/\partial V)_T \Delta V_f \approx \Delta S_{\mathrm{conf}} \qquad (16)$$

where α and β are the expansion coefficient and the isothermal compressibility, respectively. Quinn and Mandelkern[40] assumed α/β to be constant and close to the experimental value for the liquid polymer at the melting temperature (0.676 J/K/cm^3). This leads with the above volume values to a ΔS_{conf} of 7.62 J/K/mol, in good agreement with the calculations in Table III. A similar estimate (7.52 J/K/mol) was calculated by Starkweather and Boyd.[51]

Efforts to refine these calculations have revealed that the good agreement is again most likely due to a cancellation of errors.[57] A serious deviation was discovered in an attempt to include in eq 15 terms which account for the volume dependence of $(\partial P/\partial T)_V$. From paraffin data one can extrapolate[53] that for polyethylene

$$(\partial S/\partial V)_T = 9.19 - 6.72v \quad \text{(in J/K/cm}^3\text{)} \qquad (17)$$

Integration of eq 17 over the volume change on melting results in an entropy change of 4.86 J/K/mol, more than double the estimate with constant α/β. From extrapolated polyethylene melt data a similar estimate was obtained (4.54 J/K/mol).[52] The constant volume entropy of melting seems thus to be a poor approximation for the conformational entropy of fusion. The compression necessary to achieve constant volume melting seems to decrease the conformational entropy of the melt.

A different approach to an experimental determination of the conformational entropy was first suggested by Robertson.[53] In this approach one makes the assumption that the entropy of a glass at 0 K is entirely conformational. Furthermore, on heating to the glass transition temperature, the conformations remain frozen so that no increase in conformational entropy results. It would be most advantageous then to compare entropies at the glass transition temperature.

For polyethylene we have recalculated entropies based on the liquid heat capacity given in eq 11 and the crystalline and glassy heat capacities extrapolated to 100 and 0% crystallinity[47] using Simpsons rule. The crystalline entropy at 415 K is 32.68 J/K/mol of CH_2, the amorphous entropy 42.59 J/K/mol. At 0 K the remaining amorphous entropy (conformational entropy) is 4.60 J/K/mol. The increase in entropy of the glass beyond that of the crystal due to higher heat capacity between 0 and 50 K (1.04 J/K/mol of CH_2) must be completely due to nonconformational changes. The increase in entropy above the glass transition beyond that of the crystal (4.27 J/K/mol of CH_2) must, however, contain conformational changes. Assuming the fractional gain due to conformational changes is equal to that on melting (0.75) one obtains a conformational entropy change on melting at 414.6 K of 7.79 J/K/mol of CH_2 with a probable error of ±1.0 J/K/mol of CH_2. This value is in good accord with the data of Table III. Using volume rather than heat capacity for the estimate of the conformational entropy increase, Robertson[53] came to a similar value (7.49 J/K/mol of CH_2).

Conclusions

In this study of the equilibrium melting of polyethylene the following data were derived which are in accord with experiment and theory within the estimated limits quoted: melting temperature, $T_m{}^0$, 414.6 K (±0.5); crystal volume at $T_m{}^0$, 1.0038 m^3/Mg (0.9970 m^3/Mg at 298 K); amorphous volume at $T_m{}^0$, 1.2765 m^3/Mg (1.1739 m^3/Mg at 298 K); heat of fusion at $T_m{}^0$, 4.1 kJ/mol of CH_2 (±0.2); entropy of fusion at $T_m{}^0$, 9.9 J/K/mol of CH_2 (±0.4); conformational melt entropy at $T_m{}^0$, 7.8 J/K/mol of CH_2 (±1.0). Much of the controversy of melting temperature and conformational entropy in earlier literature seems to be resolved on using experimental data on temperature and volume dependence of the thermodynamic parameters and taking into account superheating on melting.

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(55) $\Delta H = -T^2\partial(\Delta G/T)/\partial T$, $\Delta S = -\partial\Delta G/\partial T$, $T_m = \Delta H/\Delta S$.
(56) The "constant" $c = R/\Delta s_f$ in eq 4 compensates greatly for the increasing value of $\ln x$. [Changing x from 12 to 620, which corresponds to a change in T_m from 255 to 410 K, $\ln x$ changes from 2.48 to 6.43, while $c \ln x$ changes only from 3.140 to 5.394, with almost no change to 355 K (3.234)].
(57) This statement is made despite the fact that for a wide range of polymers besides polyethylene such agreement with eq 15 with constant α/β has been found, and it may be of interest to inquire into the reasons as was pointed out by one of the referees to this paper (for data see, for example, A. E. Tonelli, "Analytical Calorimetry", Vol. 3, R. S. Porter and J. F. Johnson, Ed., Plenum Press, New York, N.Y., 1974, p 89).

The Scattering of Light by Uniformly Curved Rods. A Model of Semirigid Rod Macromolecules

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ABSTRACT: Uniformly curved rods may be used as a model of rodlike macromolecules which are not rigid enough to be straight rods in solution. The dependence of scattered light intensity upon scattering angle (form factor) has been obtained numerically for curved rods with angles of bend from 0 (straight rod) to 150°. The results have been used to synthesize "experimental" scattering data for rods with lengths from 1500 to 5000 Å, over the range of scattering angles accessible to conventional light-scattering photometers. The errors incurred in extrapolation of the inverse form factors to zero scattering angle are shown to be not excessive. Further, it is shown that in some circumstances the ratio of the scattered intensities at two supplementary angles is a function primarily of the contour length of the rod and does not depend strongly upon the angle of bend. Measuring such a ratio therefore gives an estimate of contour length and, if the relation between contour length and molecular weight is known, of molecular weight.

(I) Introduction

Light scattering has long been used to obtain information about molecular weights and size and shape parameters for DNA and other macromolecules.[1] Ultrasonically sheared DNA fragments, with molecular weights of the order of 10^5–10^6, have also been studied by light scattering and other techniques.[2,3] Molecular weight and mean-square radius may be obtained in principle by appropriate extrapolation of light-scattering data to the limit of zero scattering angle. In practice, the range of scattering angle accessible to conventional light-scattering photometers may not extend to sufficiently small scattering angles to permit reliable estimates of molecular weight and mean-square radius.[4,5] Interpretation of the angular dependence of the scattering is further complicated by lack of knowledge of the shapes of DNA chains. Thus, although the wormlike chain[6] is widely used as a model of DNA chains, agreement is lacking on the value of the model's