(6) (a) Lachish, U.; Williams, D. J. *Macromolecules* 1980, *13*, 1322. (b) Lachish, U.; Anderson, R. W.; Williams, D. J. *Ibid.* 1980, *13*, 1143.
(7) Triplet exciton quenching by doublet-state species is well-known in molecular crystals. See: Swenberg, C. E.; Geacintow, N. E. In "Organic Molecular Photophysics"; Birks, J. B., Ed.; Wiley-Interscience: London, 1973; section 10.2.2.6, p 499.
(8) The matrix elements for triplet–doublet energy transfer have been summarized recently: Naqvi, K. R. *J. Phys. Chem.* 1981, *15*, 2303. Note that these matrix elements are appropriate to the case that the doublet-state species be sensitized to an excited state.

Isothermal Growth of Low Molecular Weight Polyethylene Single Crystals from Solution. 1. Variation of Equilibrium Dissolution Temperature with Molecular Weight and Lamellar Thickness with Crystallization Temperature

W. M. Leung and R. St. John Manley*

Pulp and Paper Research Institute of Canada and Department of Chemistry, McGill University, Montreal, Quebec, Canada H3A 2A7

A. R. Panaras

Societê National Elf Aquitaine (Production), Centre de Recherches de Lacq, B.P. 34, 64170 Artix, France. *Received August 31, 1983*

ABSTRACT: The relation between the equilibrium melting/dissolution temperature (T_m°/T_d°), the molecular weight, the lamellar thickness, and the crystallization temperature has been investigated for linear polyethylene fractions, with molecular weights ranging from 1000 to 11 600, crystallized from dilute xylene solution. The values of T_m° and T_d° increase sharply with molecular weight and approach an asymptotic value above a molecular weight of about 5000. The measured values of T_m° are found to be in excellent accord with the values calculated from the Flory–Vrij equation. On the other hand, the observed values of T_d° are always somewhat higher than estimates from either the Pennings equation or the Sanchez–DiMarzio equation. It is found that the lamellar thickness increases continuously with crystallization temperature. This is in contrast to the behavior of low molecular weight poly(ethylene oxide) fractions which show a stepwise variation with crystallization temperature. Analysis of the observed temperature variation of the lamellar thickness, using the kinetic theory of polymer crystal growth, yields values of the interfacial free energy σ_e ranging from 20 to 60 erg/cm^2. These observed values of σ_e are low by comparison with the value of about 90 erg/cm^2 expected for high molecular weight samples. The difference may be attributed to the effects of chain ends in the interfacial regions of the crystals.

Introduction

Flexible stereoregular polymers generally crystallize from solution as lamellar structures in which the chain molecules are folded.[1,2] Although this phenomenon has been widely studied, it is still not completely understood. In the present series of papers, we propose to address the question of the origin of chain folding by studying the kinetics of crystal growth from solution, using low molecular weight fractions of polyethylene for which the transition from extended- to folded-chain growth should be observable. In this connection it is important to have accurate data on the variation of the lamellar thickness of the crystals with the temperature of crystallization and of the equilibrium dissolution temperature with molecular weight. This is the essential purpose of the present paper. Comparison of the lamellar thickness with the overall chain length provides information on the structure of the crystals by indicating whether the chains are extended or folded in the crystal lattice and the number of folds per molecule. As will be seen later, these questions are important in attempting to analyze and interpret the results of the growth rate experiments.

The lamellar thickness of single crystals of linear crystalline polymers, notably polyethylene, is generally known to increase monotonically with the temperature of crystallization (T_c).[3-6] However, in the case of low molecular weight hydroxy-terminated poly(ethylene oxide) (PEO) crystallized from the melt, the lamellar thickness increases in a stepwise manner with T_c.[7] The question arises whether a similar effect can be demonstrated in polyethylene by careful measurements on low molecular weight samples.

Previous studies of the temperature variation of the lamellar thickness of solution-grown polyethylene crystals have been mainly concerned with samples of high molecular weight. Few attempts have been made so far to systematically explore these effects for well-defined low molecular weight material.[8] In the present work we have measured the lamellar thickness of solution-grown polyethylene crystals over a wide range of crystallization temperatures for fractions ranging from 1000 to 11 600 in molecular weight. The data have been analyzed in terms of the kinetic theory of polymer crystal growth in order to derive values of the basal surface free energy.

In analysis of the experimental data a knowledge of the supercooling ($\Delta T = T_d^\circ - T_c$) or the equilibrium dissolution temperature (T_d°) (where T_c is the crystallization temperature) is critically important. T_d° is defined as the temperature at which dilute polymer solution is in equilibrium with the equilibrium (i.e., extended-chain) crystal and is dependent on the molecular weight of the polymer.[10,11] A widely used procedure to determine T_d° is to measure the dissolution temperature of crystals of various lamellar thicknesses and extrapolate the data to infinite lamellar thickness by using the Gibbs–Thompson equation.[9] This procedure will be discussed in part 2. For polyethylene, an alternative approach is used to estimate T_d° using semiempirical equations derived by Pennings[11]

0024-9297/85/2218-0746$01.50/0 © 1985 American Chemical Society

Table I
Characteristics of the Polyethylene Fractions Studied

fraction	$\bar{M}_w$	$\bar{M}_n$	$\bar{M}_w/\bar{M}_n$
PE11600	11600	11100	1.05
PE6750	6750	6100	1.10
PE4050	4050	3900	1.04
PE3100	3100	2900	1.07
PE2000		1791	
PE1000		980	

and by Sanchez and DiMarzio.[10] However, these equations do not give reliable results for low molecular weight samples. For these reasons we have devised a method for directly measuring the equilibrium dissolution temperature of crystals of the various fractions. The measurements were made by differential scanning calorimetry using suspensions of extended-chain crystals in xylene. The results are compared with values estimated from Pennings' equation[11] and the semiempirical relation of Sanchez and DiMarzio.[10]

Experimental Section

Materials. The materials used cover the molecular weight range from the paraffin dotriacontane (molecular weight 450) to 11 600. Dotriacontane was obtained from the Eastman Kodak Co. PE1000 and PE2000 were obtained from Polysciences Inc. and characterized by Springborn Laboratories, Inc., Enfield, CT. The number-average molecular weights were determined by vapor pressure osmometry. The polydispersity (M_w/M_n) is not known exactly, but analytical gel permeation chromatograms showed only a single narrow peak suggesting a fairly sharp distribution. The rest of the fractions were prepared and characterized at the Research Center of SNPA at Lacq, France. The technique of fractionation by preparative gel permeation chromatography (GPC) has been described by Peyrouset et al.[12,13] The weight-average molecular weights (M_w) were determined by analytical GPC previously calibrated by light scattering. Number-average molecular weights (M_n) were determined by vapor pressure osmometry. The molecular parameters of the various samples are given in Table I.

Measurement of the Equilibrium Dissolution Temperature ($T_d°$). By definition the equilibrium dissolution temperature is the melting point of a perfect extended-chain crystal in equilibrium with the dilute polymer solution. Accordingly the procedure used to determine $T_d°$ rests upon the following premise. The melting point of pure extended-chain crystals corresponds to the thermodynamic melting point $T_m°$ which is depressed in the presence of a solvent. Thus, the dissolution temperature of the extended-chain crystals was measured at various crystal/solvent weight fractions and the data extrapolated to infinite dilution to give $T_d°$.

The samples were retained in glass tubes (5 mm in internal diameter) which were evacuated and sealed in order to minimize oxidative degradation. The sealed tubes were placed in a silicone oil bath maintained at 150 °C for about 20 min in order to ensure complete melting of the sample. The melted sample was then quickly transferred to another thermostat set at a predetermined crystallization temperature and controlled to better than 0.05 °C. After the sample was allowed to crystallize for the desired length of time, the temperature of the thermostat was slowly lowered (at about 8 °C/h) to room temperature. The specimen, which was essentially a stack of crystals, was then removed from the glass tubes and the lamellar thickness was determined by small-angle X-ray scattering (SAXS) in order to determine the degree of chain extension.

Thermal measurements on the crystals were made on a Perkin-Elmer differential scanning calorimeter, DSC-2C. The temperature scale was calibrated with naphthalene, benzoic acid, and indium standards over the temperature range. The crystals were placed in a preweighed sample pan and weighed on a Cahn microbalance. *p*-Xylene was delivered by a microsyringe and the sample pan was then hermetically sealed. The pan was weighed again to determine the amount of solvent. At least five samples were prepared for each fraction in the concentration range 4–100% (w/w). Each sample pan was weighed again after the thermal measurement to check for leakage. The procedure for the thermal measurements was as follows. The sample was heated at 10 °C/min up to a preselected temperature which was about 10 °C below the estimated dissolution temperature. The calorimeter was allowed to remain at this temperature for 20–30 min to permit the solvent to penetrate the crystal lattice. The heating was then resumed at 0.625 or 1.25 °C/min. These low heating rates were used in order to allow annealing to produce more perfect crystals. The peak temperature was used to define the dissolution temperature and melting point of the polymer. Standard corrections were made for changes in apparent melting point and thermal resistance as a function of heating rate.[14] There is a fundamental question as to whether the peak DSC temperature measures the true melting or dissolution temperature. In general for polymers the location of this peak depends on the heating rate and sample mass. However, for the present low molecular weight extended-chain samples these problems did not arise at the very low heating rates and sample masses that were used.

Preparation of Crystals and Measurement of Lamellar Thickness. The crystallizations were carried out isothermally in *p*-xylene as solvent at temperatures (T_c) spanning the range of 65–90 °C. At higher crystallization temperatures self-seeding[15,16] was used in order to minimize the time necessary to obtain complete crystallization.

More precisely, the procedure was as follows. A suspension of the polymer was heated in an oil bath at 100 °C for 20 min in order to ensure complete dissolution. An aliquot of the solution was then transferred to a thermostat held at the crystallization temperature T_c and allowed to equilibrate. An appropriate amount of pure solvent, previously equilibrated at the crystallization temperature, was poured into the polymer solution. The time required to establish thermal equilibrium was thus minimized. The final concentration at which the crystals grew was in the range 0.02–0.5% (w/w) depending on the supercooling. The precipitate was filtered at the crystallization temperature; the resulting mats were washed with acetone and dried in vacuo at room temperature. The mats thus obtained were examined by small-angle X-ray scattering (SAXS) in order to determine the lamellar thickness of the crystals. The SAXS patterns were recorded photographically with pinhole collimation using nickel-filtered Cu K_α radiation. In all cases clearly defined low-angle reflections were observed in several orders, sometimes as high as four. Long spacings were derived from measurements on microdensitometer tracings of the SAXS patterns. The Lorentz correction was estimated to be negligible and was not applied. It should be recognized that the measured long spacings correspond to the crystalline core of the lamellae plus a disordered surface layer. When appropriate, a correction for this effect can be introduced by taking into consideration the crystallinity of the sample that can be derived from the known enthalpy of fusion (see part 2).

For all the fractions the electron diffraction patterns of crystals grown at various temperatures showed only (*hk*0) reflections. More specifically the diffraction patterns showed the complete reciprocal lattice of the (*hk*0) planes, i.e., with the three pairs of reflections (110), ($\bar{1}$10), and (200) along with their higher orders. Furthermore, for crystals exhibiting sectorization selected area diffraction from each of the four sectors showed all the (*hk*0) reflections described above. For crystals without sectorization the same diffraction pattern was observed throughout the crystals. These observations indicate that for the range of molecular weights and crystallization temperatures covered, the stems are in all cases perpendicular or nearly so to the plane of the crystals. Consequently in order to ascertain whether chain folding occurs it suffices to compare the molecular chain length with the lamellar thickness.

Results and Discussion

Equilibrium Melting and Dissolution Temperatures. The crystallization conditions and lamellar thickness of the samples used for the measurement of the equilibrium melting and dissolution temperatures are listed in Table II. Comparison of the extended-chain length with the lamellar thickness reveals that samples of PE1000,

Table II
Crystallization Conditions and Lamellar Thickness of Low Molecular Weight Polyethylene Samples

fraction	L,[a] Å	crystallizn condition	l,[b] Å	L/l
PE11600	991	1 week at 125 °C	407	2.43
PE6750	544	1 week at 125 °C	356	1.53
PE4050	348	1 week at 120 °C	299	1.16
PE3100	259	1 week at 115 °C	242	1.07
PE2000	170[c]	3 days at 110 °C	167	1.02
PE1000	117[c]	3 days at 105 °C	110	1.06

[a] Chain length. [b] Lamellar thickness. [c] Estimated from the asymptotic values of lamellar thickness of the single crystals (see Figure 6).

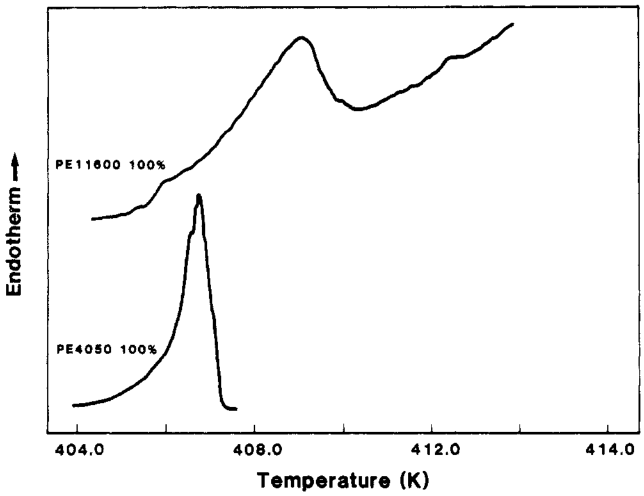

Figure 1. Typical DSC fusion curves for samples PE11600 and PE4050 at a heating rate of 0.625 °C/min. The temperature scale is adjusted for standard temperature corrections.

PE2000, PE3100, and PE4050 are composed of extended chains, but no definite statement can be made about samples PE6750 and PE11600.

Selected DSC curves are shown in Figures 1 and 2. Figure 1 shows the melting behavior of the pure PE11600 and PE4050 fractions. For PE11600 there is a major peak at 409.17 K and a small peak at 412.7 K. It is interesting to note that the temperature of the small peak agrees very well with the theoretically expected equilibrium melting temperature $T_m°$ calculated from the Flory–Vrij equation.[17] A tentative explanation of the DSC curves for this fraction may therefore be given as follows. During the crystallization at 125 °C, only a small fraction of the polymer crystallized as extended-chain crystals. The amount is not detectable by SAXS but is revealed by the small endotherm peak at 412.7 K. When the temperature was slowly decreased as described in the Experimental Section, the bulk of the polymer crystallized rapidly at a temperature somewhere below 125 °C giving crystals of undefined molecular constitution. Accordingly the major endotherm peak can be assigned to the melting of crystals of unknown molecular constitution and the smaller endotherm peak to the melting of the extended-chain crystals.

For fraction PE4050 the DSC curve shows a sharp endotherm peak with two shoulders at temperatures lower than the main peak. The temperature of the main peak corresponds closely with the expected equilibrium melting temperature for extended-chain crystals of this fraction as calculated from the Flory–Vrij equation.[17] In general, for all the pure fractions, the highest melting peak in the DSC curve could be identified as corresponding to the melting of the extended-chain crystals. Values of the equilibrium melting temperature $T_m°$ observed for the various fractions are listed in Table III and compared with the theoretically expected values calculated from the Flory–Vrij equation.

Table III
List of the Calculated and Experimental $T_m°$ and $T_d°$ Values for Various Low Molecular Weight Polyethylene Samples

	$T_m°$, K		$T_d°$, K		
fraction	Flory–Vrij eq	this work	Pennings eq	SD eq[a]	this work
dotria-contane	341.8	341.2	244.7	278.8	302.0
PE1000	386.4	386.0	325.2	338.7	352.0
PE2000	396.3	396.2	334.1	350.7	364.1
PE3100	403.5	403.7	349.2	361.9	367.4
PE4050	406.7	406.8	356.2	366.9	371.5
PE6750	411.0	410.1	366.4	374.2	376.8
PE11600	413.8	412.7	373.8	379.3	382.0[b]

[a] Sanchez–DiMarzio equation. [b] Extrapolated value.

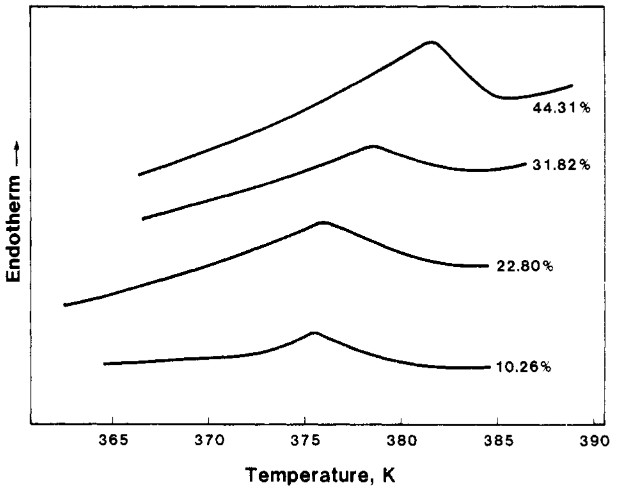

Figure 2. DSC dissolution curves of single crystals of PE4050 in the presence of xylene at various concentrations. The heating rate is 0.625 °C/min. The temperature scale is adjusted for standard corrections. The concentration is expressed as weight percent of crystals suspended in xylene.

Figure 2 shows typical endotherms for dissolution of the polyethylene fractions in xylene. In general the endotherm peaks are, as expected, broader when the polymer is in contact with solvent. It should be noted that sample PE11600 is mainly composed of crystals of undefined molecular constitution and the observed endotherm peak corresponds to the dissolution of such crystals. Consequently $T_d°$ could not be measured directly for this sample.

Plots of the dissolution temperatures as a function of concentration are shown in Figure 3. The equilibrium dissolution temperature ($T_d°$) was obtained by extrapolation of the data to zero concentration. The values thus obtained are listed in Table III. It is of interest to compare these results with theoretical estimates of $T_d°$ calculated from equations given by various authors.

From fundamental thermodynamic considerations, it can be shown[10] that the equilibrium dissolution temperature of a lamellar polymer crystal can be estimated by one of the following equations depending on the assumptions made in deriving an expression for the free energy difference between liquid polymer and crystal:

$$T_d° = T_m°[1/(1 - \gamma)] \quad (1)$$

$$T_d° = T_m°[\gamma + (1 + \gamma^2)^{1/2}] \quad (2)$$

$$T_d° = T_m°(1 + \gamma) \quad (3)$$

where $T_m°$ is the equilibrium melting temperature and

$$\gamma = RT_m° \ln a_u(T_d°)/\Delta H_u(T_m°)$$

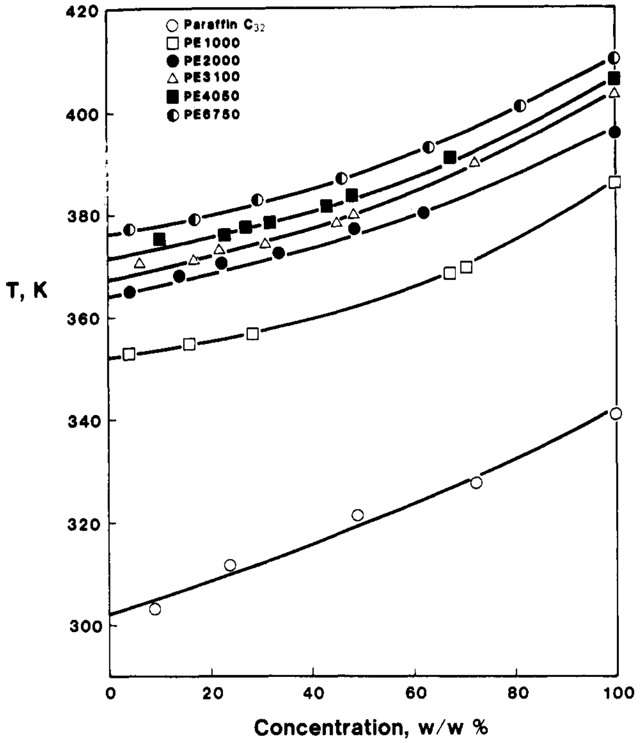

Figure 3. Plots of dissolution temperature in the presence of xylene as a function of concentration for the various fractions of polyethylene. The concentration is expressed as weight percent of crystals.

where a_u is the activity which is a measure of the polymer/solvent interaction and ΔH_u is the heat of fusion per mole of monomer.

These equations show that $T_d°$ depends on two variables, $T_m°$ and a_u, which are molecular weight dependent. The molecular weight dependence of $T_m°$ has been estimated.[17-19]

Pennings[11] has given a method for determining a_u. For dilute solutions his equation is

$$\ln a_u = \frac{V_u}{V_1}\left[\frac{\ln v_2 + 1}{x} - \left(\frac{1}{2} + \frac{V_1 A_2}{\bar{v}_2^{\,2}}\right)\right] \qquad (4)$$

where A_2 is the second virial coefficient, $\bar{v}_2$ is the partial specific volume of the polymer, v_2 is the volume fraction of the polymer, V_1 is the molar volume of the solvent, V_u is the molar volume of the monomer unit, and x is the ratio of the molar volumes of the polymer and solvent. Pennings[11] and Krigbaum and Trementozzi[18] have estimated A_2 from osmotic pressure measurements of polyethylene in xylene as a function of molecular weight. The Pennings relation between A_2 and molecular weight (M) is

$$A_2 = 1.45 \times 10^{-3} + 0.29M^{-0.5} \qquad (5)$$

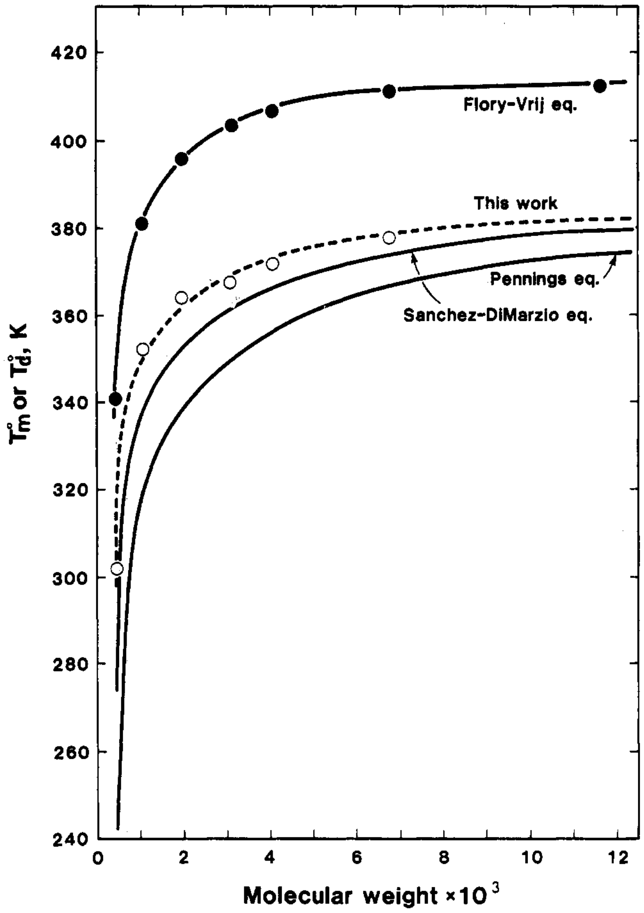

Figure 4. Comparison of the molecular weight dependence of $T_m°$ and $T_d°$, as measured in the present work, with the relationship estimated from the Flory–Vrij equation, the Pennings equation, and the Sanchez–DiMarzio equation. For the $T_m°$/molecular weight relation the data points are the observed values while the curve is calculated from the Flory–Vrij equation.

Sanchez and DiMarzio[10] have shown that the dependence of $T_d°$ on the approximate form of eq 1–3 is weak. We have calculated values of $T_d°$ from eq 2 and the Pennings relations, eq 4 and 5, using the following input data: ΔH_u = 980 cal/mol, $V_1/\bar{v}_2^{\,2}$ = 87.0 g^2/(mL mol), V_1/V_u = 7.73, and $v_2 = 10^{-4}$. Values of $T_m°$ were calculated from the Flory–Vrij equation.[17] The results are tabulated in Table III. (In accordance with normal practice in work of this kind we have used the following units in this series of papers: crystallization temperature T_c in degrees Celsius (°C), lamellar thickness l in angstrom units (Å), the heat of fusion in erg/cm^3 or cal/g, surface free energies σ and σ_e in units of erg/cm^2, gas constant R = 1.987 cal/(mol K). The conversion factors to SI units are 0 °C = 273.16 K, 1 Å = 10^{-1} nm = 10^{-10} m, 1 erg/cm^3 = 0.1 J/m^3, 1 cal/g = 4.184 J/g, 1 erg/cm^2 = 1 mJ/m^2, 1 cal/mol = 4.184 J/mol, and R = 8.314 J/(mol K).)

Sanchez and DiMarzio[10] have proposed the following semiempirical relation for $T_d°$ for polyethylene in xylene:

$$T_d° = [T_m° - 29 + \tau_d°]/2 \qquad (6)$$

where $T_m°$ and $\tau_d°$ are respectively the Flory–Vrij estimates for the equilibrium melting temperature and the Pennings estimates for the equilibrium dissolution temperature. Values of $T_d°$ calculated from eq 6 are also listed in Table III. In Figure 4 the measured values of $T_d°$ and $T_m°$ are shown as a function of molecular weight and compared with estimates from the Pennings, Sanchez–DiMarzio, and Flory–Vrij equations, respectively. It is seen that the measured values of $T_m°$ obtained in the present work are in good agreement with the values given by the Flory–Vrij equation. At low molecular weights the difference is insignificant. At molecular weights of 6750 and 11 600 the observed value of $T_m°$ is about 1 K lower than the theoretical value. This excellent agreement may seem somewhat surprising since the Flory–Vrij equation was derived for molecular crystals where the molecules have exactly the same length. This situation is not normally obtained in any real polymer system. The good agreement implies that, in the low molecular weight range of interest here, small deviations from monodispersity can be tolerated by the theory. On the other hand, the measured values of $T_d°$ are considerably higher than those estimated from either the Pennings or Sanchez–DiMarzio equation.

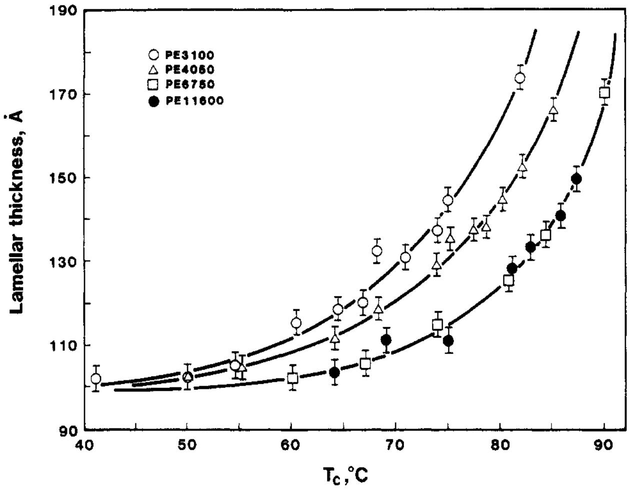

Figure 5. Lamellar thickness as a function of crystallization temperature for various low molecular weight polyethylene single crystals.

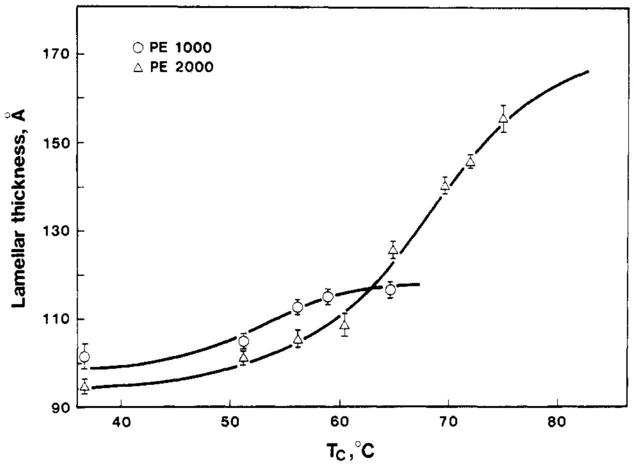

Figure 6. Lamellar thickness as a function of crystallization temperature for single crystals of PE1000 and PE2000.

Table IV
Lamellar Thickness of Low Molecular Weight Polyethylene Single Crystals at Various Crystallization Temperatures

sample	T_c, °C	l, Å	sample	T_c, °C	l, Å
PE1000	36.6	101	PE2000	36.6	95
	51.2	105		51.2	101
	56.2	114		56.2	106
	58.9	115		60.5	109
	64.6	117		65.0	125
				69.7	140
				72.0	145
				75.1	155
PE3100	40.2	104	PE4050	50.0	103
	49.9	105		55.0	106
	54.9	106		64.5	113
	60.4	116		68.4	120
	64.5	119		73.8	129
	66.8	121		75.1	137
	71.0	131		77.4	138
	74.0	137		80.2	144
	75.0	144		82.2	153
	82.2	174		85.2	165
PE6750	60.1	103	PE11600	64.0	103
	67.0	105		69.0	111
	74.0	115		75.1	113
	80.9	126		81.0	128
	84.5	136		82.9	133
	90.0	170		85.7	140
				87.3	149

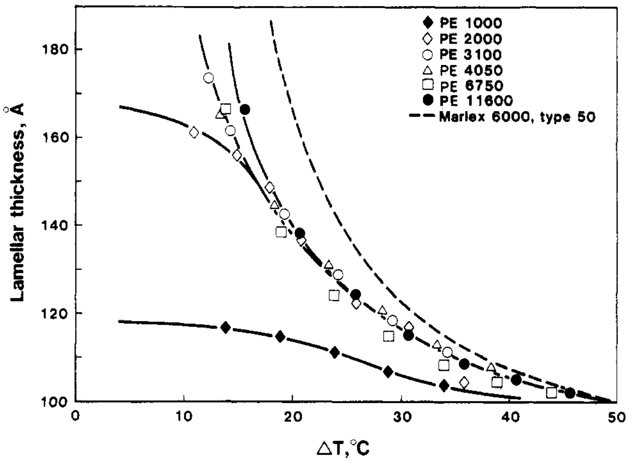

Figure 7. Lamellar thickness as a function of supercooling ($\Delta T = T_d° - T_c$) for polyethylene single crystals of various molecular weights. The data for Marlex 6000 are taken from the literature (see ref 9).

The lower the molecular weight, the greater is the difference. The discrepancy is not surprising since Pennings[11] has already noted that the expression for the second virial coefficient, A_2, breaks down for low molecular weights, probably because of the neglect of the temperature dependence of A_2.

Variation of Lamellar Thickness with T_c. Figures 5 and 6 show the dependence of the long spacing on the crystallization temperature for the various molecular weight fractions studied. The experimental data are listed in Table IV. For the four fractions with molecular weights from 3100 to 11 600 the principal trend is the apparently continuous increase of the long spacing with crystallization temperature. For these fractions all the curves seem to show a limiting long spacing at lower crystallization temperatures, while at higher temperatures the curves are displaced from each other in such a manner that the crystallization temperature required to produce crystals with a given long spacing increases with molecular weight. This behavior is consistent with the known fact that for a given chain length the long spacing depends on the reciprocal supercooling ($\Delta T = T_d° - T_c$) and shorter chains are expected to have a lower equilibrium dissolution temperature.

Considering now the fractions with molecular weights of PE1000 and PE2000, the long spacing tends progressively toward a limiting value near the length of the extended chain. It is interesting to note that for sample PE1000 significant departures from the classical ΔT relation are observed (see Figure 7). This behavior has already been predicted by Mandelkern et al.[20] using nucleation theory pertinent to chains of finite length.

The temperature variation of the long spacing for fractions PE1000 and PE2000 suggests a model in which the terminal portions of the chains are excluded from the crystal interior, leading to cilia dangling from the basal surfaces of the lamella. This model is consistent with the findings of Keller and Priest[21] that about 90% of the chain ends are localized on the fold surfaces of solution-grown polyethylene crystals. For the present low molecular weight samples the asymptotic approach of the long spacing to full chain extension indicates that the degree of surface disorder in these crystals decreases with increasing crystallization temperature.

For the low molecular weight polyethylene samples the apparently continuous increase of the long spacing with crystallization temperature is at variance with the behavior of low molecular weight hydroxy-terminated poly(ethylene oxide) fractions crystallized from the melt. For this case it has been reported that the long spacing increases discontinuously with T_c.[7] The long spacings of such crystals show that the chains are either fully extended or folded a small integral number of times. The chain ends are thus localized in the surface layers of the lamellae. The lamellar thickness is therefore an integral submultiple of the overall chain length. It has been suggested that this behavior is due to strong attractive forces (hydrogen bonds) between the hydroxyl end groups resulting in end-group pairing. Thus, a stepwise or discontinuous increase in lamellar thickness with T_c would not be expected in polymers, such as polyethylene, where there can be no association of the end groups. Nevertheless, it is interesting to consider whether a stepwise change in lamellar thickness could have remained undetected by the SAXS measurements. If one takes into consideration the chain length of the various fractions used in the present work, the number of stem lengths per molecule can be readily estimated for the crystals over the accessible range of crystallization temperatures. For this purpose we have taken the length of the CH_2 unit in the planar zigzag conformation as 0.125 nm and the molecular mass of the CH_2 unit as 14. The mean extended-chain length is therefore $1.25(M_n/14)$ Å. For example, for PE3100 the extended-chain length is 259 Å and over the temperature range investigated the lamellar thickness changes from 104 to 174 Å, which, assuming rejection of fractional stems from the crystal lattice,[21] corresponds to a change from one to two stems per molecule. Thus, if the chain ends were localized on the lamellar surfaces and the change from one to two stems per molecule occurred in a stepwise manner, the change in long spacing would have been 130 Å, which is sufficiently large to be easily detected by SAXS. A similar conclusion can be drawn for sample PE 4050, but for samples PE6070 and PE11600 a discontinuous change in the lamellar thickness could not be easily detected by SAXS because of the small incremental change in each step. Accordingly, if we take the favorable case of the fractions PE3100 and PE4050, it seems reasonable to conclude that the observed apparent continuous increase of the lamellar thickness with T_c is substantially correct. As will be seen later these considerations are important in attempting to interpret the growth rate data to be presented in part 3.

Basal Surface Free Energy (σ_e). According to the kinetic theory of polymer crystal growth from solution, the initial thickness (l_g^*) of a chain folded lamella is of the form

$$l_g^* = 2\sigma_e T_d^\circ/\Delta h_f(\Delta T) + \delta l \qquad (7)$$

where σ_e is the fold surface free energy, i.e., the work involved in the formation of a unit area of folded surface; T_d° is the equilibrium dissolution temperature; $\Delta T = T_d^\circ - T_c$ is the degree of supercooling corresponding to the crystallization temperature T_c; Δh_f is the bulk enthalpy of fusion per unit volume, and δl is an approximately constant term whose explicit form is different in various theories. According to eq 7 a plot of l_g^* against $T_d^\circ/\Delta T$ should be linear and have a positive intercept of δl on the l_g^* axis and a slope of $2\sigma_e/\Delta h_f$. Thus, if Δh_f is known, σ_e can be determined.

It is important to recognize that eq 7 is derived on the assumption that the molecular chain length greatly exceeds the lamellar thickness. This requirement is clearly not satisfied by the low molecular weight species being studied here, for which the chain length is comparable to the lamellar thickness. Thus, a question arises as to the significance of the σ_e values that are obtained. In approaching this question we shall proceed by testing the equation in order to ascertain whether there is a lower limit of molecular weight where it fails to give reasonable values of σ_e that are in good agreement with the values obtained by other independent methods. This will be done later when growth rate and thermodynamic data are presented (parts 2 and 3).

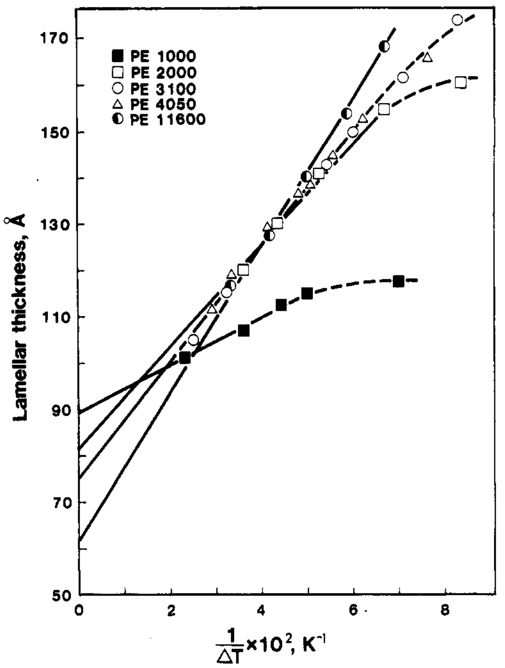

Figure 8. Plots of lamellar thickness vs. reciprocal supercooling for single crystals of various low molecular weight polyethylene fractions.

Table V
Values of the Basal Surface Free Energy σ_e and the Intercept Obtained from the Plots of l vs. $1/\Delta T$

sample	σ_e, erg/cm^2	δl, Å
PE1000	20.4	89.3
PE2000	42.1	81.5
PE3100	48.9	75.2
PE4050	48.5	75.2
PE6750	51.7	71.1
PE11600	60.1	61.5

It may be noted that polymer crystals are essentially unstable and slowly increase in thickness spontaneously at the crystallization temperature. This time-dependent process is often encountered in crystallization from the supercooled melt.[22-25] However, for solution-grown polyethylene single crystals it has been shown that there is no change in the crystallite thickness or thermodynamic stability, during either the crystallization process or subsequent storage for long periods of time, if the crystallization temperature is maintained constant.[26] This seems to suggest that isothermal thickening is virtually absent at the temperatures involved in crystallization from dilute solution. Accordingly for present purposes it is assumed that the measured lamellar thickness can be identified with the initial fold length as predicted by the theories. Direct experimental evidence from the present work will be presented later (part 3) to support this assumption.

Figure 8 shows the results that are obtained when the long spacing data for the various fractions are plotted according to eq 7. For samples PE3100 to PE11600 eq 7 is obeyed within the experimental error, giving an intercept δl of 60–75 Å. This may be compared with the value of 43–55 Å obtained with higher molecular weight polyethylene samples crystallized from xylene.[27] If we take $\Delta h = 2.80 \times 10^9$ erg/cm^3, the values of σ_e obtained as shown in Table V are in the range 50–60 erg/cm^2. These values are much lower than the 90 erg/cm^2 that is considered to be the upper limit of this parameter.[27] In this connection it is pertinent to emphasize that σ_e is known to depend on chain length for low molecular weights and reaches the asymptotic value of 90 erg/cm^2 at high molecular weight.[28,29] The observed values of σ_e are therefore well within the anticipated range.

For samples PE1000 and PE2000 the plots of l_g^* vs. $1/\Delta T$ show deviations from linearity at low supercooling ΔT. This is probably related to the fact that l_g^* reaches an asymptotic value at low supercooling where the lamellar thickness and the chain length become equal. From the slope of the linear portion of these curves at higher supercooling we calculate a value of $\sigma_e = 20$ erg/cm^2 for sample PE1000 and $\sigma_e = 42$ erg/cm^2 for PE2000. The crystals of sample PE1000 are essentially extended-chain crystals and hence the low value of σ_e for this sample undoubtedly reflects the exclusive contribution of the chain ends. The value of $\sigma_e = 42$ erg/cm^2 for PE2000 suggests that this sample contains some folds in spite of its short chain length. It may be well to note, however, that these statements are based on eq 7, which may be inaccurate at such low molecular weights. Accordingly the absolute values of σ_e for the crystals of these two fractions should be considered with caution.

Conclusions

The equilibrium melting ($T_m°$)/dissolution ($T_d°$) temperatures of low molecular weight polyethylene fractions have been determined directly by calorimetric measurements on macroscopic extended-chain crystals. The measured values of $T_m°$ are in good agreement with the theoretically expected values calculated from the Flory–Vrij equation. For $T_d°$ the calorimetrically measured values are somewhat higher than those predicted by the relations of Pennings and Sanchez–DiMarzio but, as will be shown in part 2, they are in good accord with values obtained from thermodynamic measurements.

When the same low molecular weight fractions are crystallized from dilute solution, the long spacing or lamellar thickness increases continuously with crystallization temperature. The chains thus undergo a gradual unfolding as the supercooling decreases. This implies that the chain ends either must be located outside the lamellae where they dangle as cilia of variable length or are incorporated into the crystal lattice. The former interpretation would be consistent with the finding of Keller and Priest[21] that in polyethylene single crystals 90% of the chain ends are localized on the basal surfaces.

The observed behavior of these low molecular weight polyethylenes stands in sharp contrast to that of low molecular weight poly(ethylene oxide) single crystals grown from the melt where the chain ends are preferentially rejected onto the lamellar surfaces so that the folding occurs in a quantized manner.

Analysis of the observed temperature variation of the lamellar thickness for these low molecular weight polyethylene fractions, using the kinetic theory of polymer crystal growth, yields values of the basal surface free energy of 20–60 erg/cm^2. These values are within the anticipated range.

Acknowledgment. We thank Professors A. J. Kovacs and J. D. Hoffman for constructive discussions and critical comments on this work. We also gratefully acknowledge the support of the National Science and Engineering Research Council of Canada and the Ministère de l'éducation du Québec.

References and Notes

(1) A. Keller, *Philos. Mag.*, **2**, 1171 (1957).
(2) E. W. Fischer, *Z. Naturforsch. A*, **12**, 753 (1957).
(3) A. Keller and A. O'Connor, *Discuss. Faraday Soc.*, **25**, 114 (1958).
(4) A. Nakajima, F. Hamada, S. Hayashi, and T. Sumida, *Kolloid Z. Z. Polym.*, **222**, 10 (1968).
(5) A. Nakajima, S. Hayashi, T. Korenaga, and T. Sumida, *Kolloid Z. Z. Polym.*, **222**, 124 (1968).
(6) T. Kawai and A. Keller, *Philos. Mag.*, **11**, 1165 (1965).
(7) J. P. Arlie, P. Spegt, and A. Skoulios, *Makromol. Chem.*, **104**, 212 (1967).
(8) A. Keller and Y. Udagawa, *J. Polym. Sci., Part A2*, **10**, 221 (1972).
(9) T. W. Huseby and H. E. Bair, *J. Appl. Phys.*, **39**, 4969 (1968).
(10) I. C. Sanchez and E. A. DiMarzio, *Macromolecules*, **4**, 677 (1971).
(11) A. J. Pennings in "Characterization of Macromolecular Structure", Publication No. 1573, National Academy of Sciences, Washington, DC, 1968, p 214.
(12) A. Peyrouset and R. Panaris, *J. Appl. Polym. Sci.*, **16**, 315 (1972).
(13) A. Peyrouset, R. Prechner, R. Panaras, and H. Benoit, *J. Appl. Polym. Sci.*, **19**, 1363 (1975).
(14) Perkin-Elmer, Instruction Manual for the Model DSC-2C Differential Scanning Calorimeter.
(15) D. J. Blundell, A. Keller, and A. J. Kovacs, *J. Polym. Sci., Part B*, **4**, 481 (1966).
(16) D. J. Blundell and A. Keller, *J. Macromol. Sci., Phys.*, **B2**, 301 (1968).
(17) P. J. Flory and A. Vrij, *J. Am. Chem. Soc.*, **85**, 3548 (1963).
(18) W. R. Krigbaum and Q. A. Tremontozzi, *J. Polym. Sci.*, **28**, 295 (1958).
(19) M. G. Broadhurst, *J. Res. Natl. Bur. Stand., Sect. A*, **70**, 481 (1966).
(20) L. Mandelkern, J. G. Fatou, and C. Howard, *J. Phys. Chem.*, **68**, 3386 (1964).
(21) A. Keller and J. D. Priest, *J. Macromol. Sci., Phys.*, **B2**, 479 (1968).
(22) J. J. Weeks, *J. Res. Natl. Bur. Stand., Sect. A*, **67**, 441 (1963).
(23) J. D. Hoffman and J. J. Weeks, *J. Chem. Phys.*, **42**, 4301 (1965).
(24) J. Dlugosz, G. V. Fraser, D. Grubb, A. Keller, J. A. Odell, and P. L. Goggin, *Polymer*, **17**, 471 (1976).
(25) A. J. Kovacs, A. Gonthier, and C. Straupe, *J. Polym. Sci., Part C*, **50**, 283 (1975).
(26) J. F. Jackson and L. Mandelkern, *J. Polym. Sci., Part B*, **5**, 557 (1967).
(27) J. D. Hoffman, G. T. Davis, and J. I. Lauritzen, Jr., in "Treatise on Solid State Chemistry", Vol. 3, Chapter 7, N. B. Hannay, Ed., Plenum Press, New York, 1976.
(28) J. D. Hoffman, L. J. Frolen, G. S. Ross, and J. I. Lauritzen, Jr., *J. Res. Natl. Bur. Stand., Sect. A*, **79**, 671 (1975).
(29) L. Mandelkern, A. L. Allou, Jr., and M. Gopalan, *J. Phys. Chem.*, **72**, 309 (1968).