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Melting behaviour of low molecular weight poly (ethylene-oxide) fractions

2. Folded chain crystals

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With 15 figures and 3 tables

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Introduction

Low molecular weight fractions of hydroxy-terminated poly (ethylene-oxide) (PEO) crystallise with molecules either fully extended or folded only a small integer number, *n*, of times (1–3). It follows that chain ends must be rejected onto the surface layers of the crystalline lamellae. Consequently, during crystallisation or annealing folded chain PEO crystals do not show a gradual increase in crystal thickness with increasing temperature and/or time. Instead, their thickness increases stepwise according to the reduction in the number of folds per molecule (4, 5).

n-times folded chain PEO crystals are *metastable* with respect to (*n*–1)-times folded ones and even more so to extended chain crystals. They thus have greater thermal stability than usually found for folded chain polymer crystals which are *unstable* rather than metastable. The unusual thermal stability of these folded chain PEO crystals makes them ideal for investigating melting behaviour, e.g. by differential scanning calorimetry (DSC), since chain unfolding during heating which usually makes the interpretation of thermograms uncertain (6), either does not occur or occurs in an unambiguous manner.

In the present study this behaviour has been exploited to measure the rate of chain unfolding both at constant temperature and during uniform heating and to define a reliable stability criterion for folded chain crystals. Furthermore, by applying the theoretical analysis of melting proposed in the first paper of this series (7) to the data obtained with folded chain PEO crystals, a reasonable estimate could be derived for the respective surface free energy contributions of chain ends and chain folds. The analysis leads to an estimate of the average length of the cilia associated with the chain ends and to that of chain folds. Finally, the classical method for determining the value of the surface free energy from melting point and crystal thickness measurements is critically examined in order to bring new light on the melting behaviour of folded chain polymer crystals in general.

Experimental

The PEO samples, used in previous work (5, 7), were commercial OH-terminated low

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molecular weight fractions supplied by Union Carbide (prefix C), Hoechst (H) or Fluka (F). Their molecular weights and average chain lengths $\lambda = M_n/\nu$ are listed in tab. 1, ν being the molar mass per unit length (158.2 g/nm) along the crystal *c* axis (8).

Tab. 1. Molecular parameters of the PEO fractions studied ($\nu = 158.2$ g/nm)

Polymer	M_n	M_ω/M_n	$\lambda = M_n/\nu$ (nm)
F 3000	2780	1.08	17.57
H 4000	3900	1.11	24.65
H 6000	5970	1.06	37.74
C 8000	7760	1.19	49.05
H 10000	9970	1.20	63.02

The samples were stored in powdered form *in vacuo* over P_2O_5 for several months before being used. For DSC studies, specimens were weighed into sealable aluminium capsules of the type intended for volatile liquids using a Cahn electrobalance, reading to 5×10^{-6} g. Routinely, specimen mass *m* was arranged to be $(3.6 \pm 0.1) \times 10^{-3}$ g.

The powder specimens in still open capsules were then further stored *in vacuo* over P_2O_5 for a period of at least one hour after which the capsules were rapidly sealed. They were then stacked in closed copper tubes, in the presence of dry silica gel, for the duration of the thermal treatment and subsequent crystallisation. This was carried out in constant temperature water-baths, whose fluctuations were less than ±0.02 deg C over periods of up to one week. Temperatures were measured with a Hewlett-Packard quartz thermometer accurate to within 0.02 deg C.

Two alternative crystallisation procedures were employed.

1) Specimens of F 3000 and H 4000 were melted at 70 °C for 5 min. and then isothermally crystallised at a temperature T_c for a time t_c, after which they were quenched in a dry-ice/acetone mixture.

2) On the other hand, samples H 6000, C 8000 and H 10000, were *self-seeded* (9) in order to minimise the period necessary to reach complete crystallisation at high T_c values. For these specimens the following thermal treatment was employed:

$$70\,°\mathrm{C}\,(5\ \mathrm{min.}) \rightarrow 25\,°\mathrm{C}\,(10\ \mathrm{min.}) \rightarrow T_s\,(15\ \mathrm{min.}) \rightarrow T_c(t_c)$$

where the "seeding" temperature T_s was chosen appropriately for each sample. Again, following isothermal crystallisation at T_c, specimens were quenched in a dry-ice/acetone mixture. For each set of crystallisation conditions several specimens were prepared and each used only once.

The melting behaviour of the different fractions was studied using a Perkin-Elmer Differential Scanning Calorimeter (model DSC-1 B).

During operation the sample chamber was continually flushed with dry, oxygen-free nitrogen. The specimen capsule and an empty reference capsule were heated at constant rate *s* (scan speed) through the melting range while recording the differential heat flux $\dot{Q}$. The apparent melting point(s) T_p and enthalpy of fusion ΔH were determined respectively from the peak temperature(s) and the total area of the melting endotherm. Nominal heating-rates of 0.5, 1, 2, 4, 8, 16 and 32 deg C/min were used. Stop-watch measurements, however, showed the true values of *s* to be (4.2 ± 0.2) % greater than their nominal values.

The specimen temperature in the capsule is known to be less than the measured temperature by $R_0\dot{Q}$, where R_0 is the thermal resistance of the capsule/sample-holder contact (10). The value of T_p was therefore derived from the temperature of the endotherm peak by subtracting $R_0\dot{Q}_{\max}$ ($\leqslant 0.2$ deg. C for $s = 0.5$ deg C/min.), where $\dot{Q}_{\max}$ is the peak value of $\dot{Q}$. Similarly, temperatures at all points on the endotherms shown in this paper (figs. 3 and 5) have been reduced by $R_0\dot{Q}$. R_0 was determined from 16 melting measurements of ca. 2×10^{-3} g of indium to be 3.6 ± 0.1 deg min/cal.

The temperature scale of the calorimeter was calibrated daily, using 10^{-3} g specimens of p-nitrotoluene ($T_m = 51.54$ °C) and naphthalene ($T_m = 80.20$ °C), assuming T_p measured at $s = 0.5$ deg C/min to be equal to the melting temperature T_m. With these procedures it was found that precision of T_p measurements was better than ±0.2 deg C for repeated experiments on different specimens, but better than ±0.02 deg C on the same specimen.

The differential heat flux ($\dot{Q}$) scale was calibrated using the enthalpy of fusion ΔH of benzoic acid (11). Precision of ΔH measurements was found to be ±1.5 %. The level of instrumental noise on the output signal $\dot{Q}$ varied greatly from day to day, but was always less than 0.001 cal/min. In the endotherms of figs. 3 and 5, $\dot{Q}$ has been normalised for specimen mass and heating-rate by plotting as the specific heat $C_p = \dot{Q}/m.s$ in cal/g. deg C. In addition, the smoothed baseline level of C_p has been subtracted in order to allow easy comparison of the melting peaks.

Stability of folded chain PEO crystals

Preliminary experiments were carried out to determine the thermal stability of folded chain PEO crystals during heating at various rates.

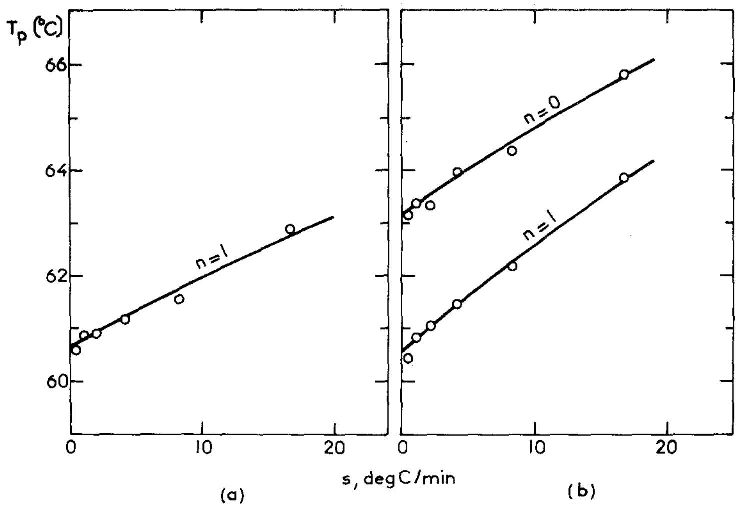

Fig. 1. Melting peak temperatures T_p versus heating-rate *s* for PEO H 6000 crystals in (*a*) once folded and (*b*) partly extended and partly once folded chain form.

Stable Crystals

Firstly, specimens of H 6000 were fully crystallised at $T_c = 51.00$ °C ($t_c = 1$ h), after self-seeding at $T_s = 62.45$ °C. Small-angle X-ray scattering shows that at 51 °C, H 6000 crystallises in the *once folded chain form* (2). These specimens were then melted in the DSC at different heating rates *s*. For all values of *s*, between 0.5 and 32 deg C/min, only a single melting peak was observed. Furthermore, as shown in fig. 1a, T_p increased monotonically with *s* in the manner typical of simple substances, as illustrated in fig. 2 for benzoic acid. Other simple substances such as p-nitrotoluene, naphthalene, adipic acid and indium showed entirely analogous behaviour. The monotonic rise in T_p with increasing *s* is caused essentially by thermal inertia of the specimen (10) and possibly by the finite melting rate of the crystals (12, 13).

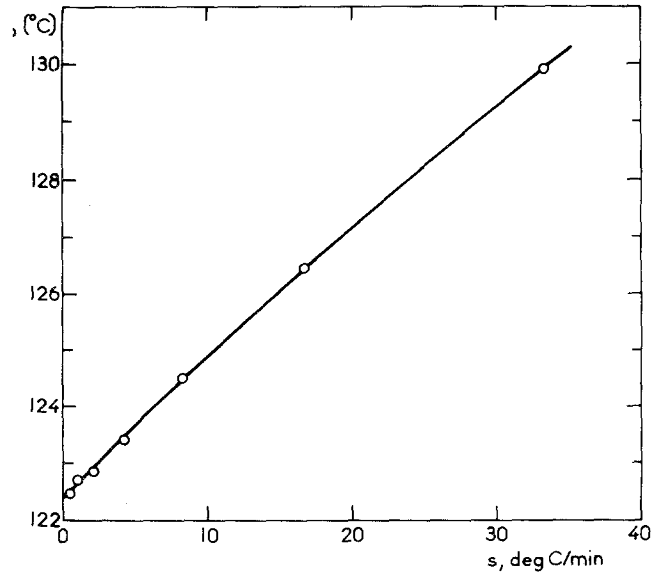

Fig. 2. Melting peak temperature T_p versus *s* for benzoic acid

Secondly, specimens of H 6000 were fully crystallised at $T_c = 57.0$ °C ($t_c = 20.3$ h), again after self-seeding at $T_s = 62.45$ °C. Under these conditions about 36% of the once folded chain crystals grown at 57 °C transform into the extended chain form (see below). In fact the melting endotherm of these specimens showed two distinct melting peaks at all values of *s*. These can thus be assigned to the melting of once folded (lower T_p) and extended chain (upper T_p) crystals. As shown in fig. 1b each peak temperature again increased monotonically with *s*, as for simple substances. Nevertheless, the ratio of the areas under the two peaks was independent of *s*.

If chain unfolding (crystal thickening) occurred during heating in the DSC, it would appear in one of two ways.

1. In the case of *stepwise* crystal thickening, one would observe two distinct melting peaks with a decreasing proportion of the second (high temperature) peak area as compared to the first when *s* increases.

2. If thickening of folded chain crystals occurred *gradually* on heating, as usually observed for other polymers (6), one would observe only one peak with the characteristic upturn of T_p as s decreases towards zero. Stepwise thickening may give rise to similar effect if the peak temperatures are close enough to make the two peaks merge (see below).

Since neither of these features was observed, clearly once folded chain H 6000 crystals do not unfold appreciably during heating but remain essentially in their native form until completion of their melting, at least for $s \geqslant 0.5$ deg C/min. This is consistent with the direct observations made on individual crystals (5, 13, 14) which showed that chain extension for this sample proceeds very slowly over the whole temperature range. Similar behaviour was observed for once folded chain C 8000 and H 10000 and for twice folded chain H 10000 crystals, suggesting that the stability criterion during heating involves some critical crystal thickness, as discussed below.

Figs. 1 and 2 show that the extrapolated value of T_p at $s = 0$, *i.e.* the true melting point T_m, is indistinguishable within experimental error from the T_p value measured at $s = 0.5$ deg C/min. On a routine basis therefore $T_p (s = 0.5)$ was assumed identical to T_m, at least for „stable" crystals.

Unstable crystals

When chain unfolding did occur during heating in the DSC it was quite unmistakable. The effect was most clearly resolved during melting of once folded chain crystals of H 4000 obtained at $T_c < 47.5$ °C. In this case a second quite separate higher temperature endotherm peak appeared corresponding to melting of extended chain crystals: its area increased at the expense of the lower temperature peak as s was reduced. As mentioned above, this behaviour is characteristic of stepwise unfolding during heating. Direct observation on once folded chain H 4000 crystals showed in fact that the rate of chain extension is at least 50 times greater than that of once folded chain H 6000 crystals (14).

Melting endotherms typical of H 4000 crystallised below 47.5 °C are shown in fig. 3, for $T_c = 42.9$ °C. As s increases the two peaks merge together because their widths increase with s due to thermal inertia effects (10). Note the absence of any exothermic peak during the thickening process, suggesting that chain unfolding does not involve large-scale melting followed by recrystallisation. Instead, these two processes occur simultaneously as evidenced by microscopic observations (13).

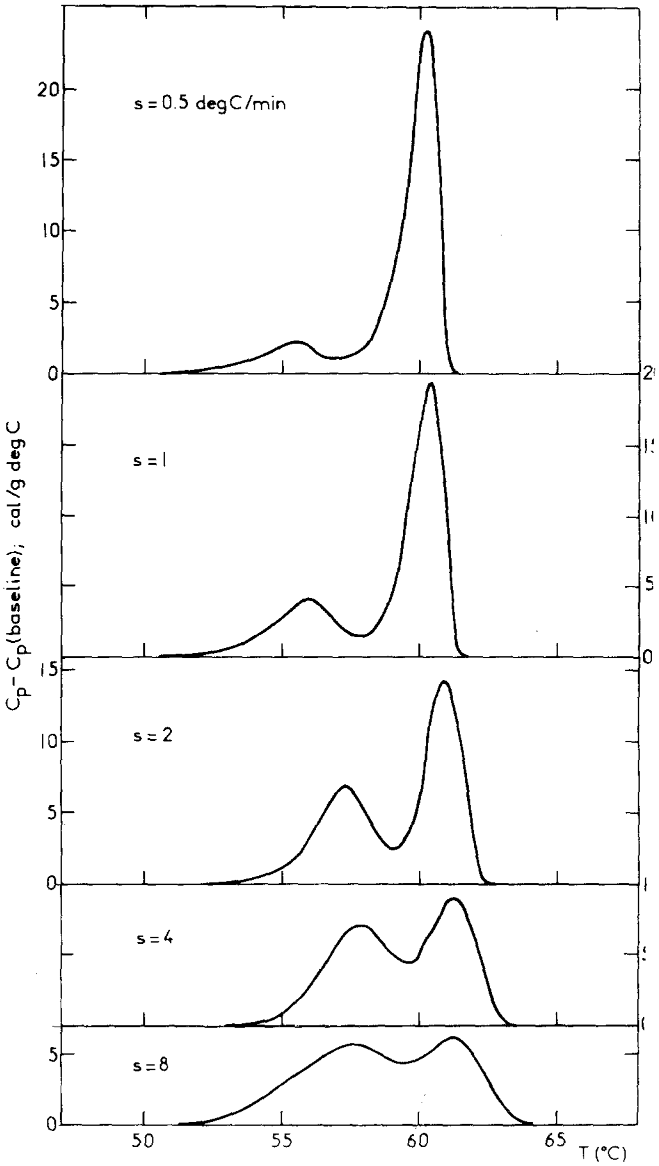

Fig. 3. Melting endotherms obtained at different heating-rates s for PEO H 4000, crystallised at $T_c = 42.9$ °C in once folded chain form ($t_c = 2.5$ h)

Twice folded chain crystals of C 8000 showed similar behaviour. In this case, however, the melting peaks were too closely spaced in temperature, making resolution of the individual peaks impossible for samples of the usual mass. Fair resolution could be obtained by reducing the specimen mass (to 6×10^{-4} g) to decrease thermal inertia, thus sharpening individual peaks.

Three-times folded chain crystals of H10000 also undergo chain unfolding during heating. In this case the peaks are so closely spaced that they overlap even with samples of reduced mass. Their presence was however inferred from the following experiment. Specimens of 6×10^{-4} g were melted at 70 °C and then quenched into the range of room temperature. Melting peak temperatures of these specimens exhibited the characteristic upturn of T_p with decreasing s, as shown in fig. 4. This behaviour clearly indicates the presence of folded chain crystals undergoing an increasing amount of chain unfolding during heating as s decreases (6).

In addition H 10000 quenched to room temperature is known to crystallise in the three-times folded chain form (2). It can thus be reasonably inferred that the peak observed at values of $s \geqslant 4$ deg C/min corresponds to the melting of such crystals, since in this range T_p increases with s (fig. 4) in the manner characteristic of stable crystals. This interpretation is consistent with the observation by *Spegt* (4) that three-times folded chain crystals of H 10000 transform to the twice folded form in less than 3 min., when annealed at, or above 55 °C, while the subsequent transformation into the once folded chain conformation requires several hours.

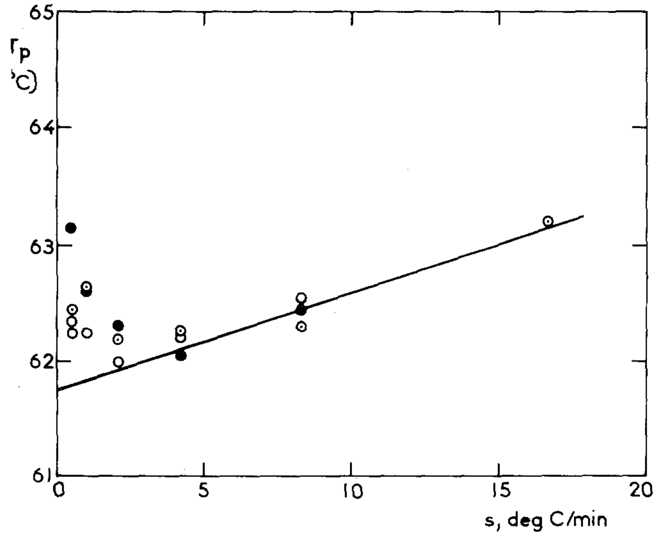

Fig. 4. Melting peak temperature T_p versus s for specimens of reduced mass (6.10^{-4} g) of PEO H 10000, crystallised in three-times folded chain form; ○: $T_c = 23$ °C, ⊙: $T_c = 24$ °C and ●: $T_c = 29$ °C

Accordingly the melting point of the three-times folded chain H 10000 crystals was estimated by extrapolating to $s = 0$ the T_p values obtained for $s \geqslant 4$ deg C/min, as shown in fig. 4. The same extrapolation procedure was employed for determining T_m values of once folded chain H 4000 and twice folded chain C 8000 crystals, using the appropriate lower melting peak temperatures obtained with specimens of reduced mass.

Finally, similar investigations on quenched specimens of F 3000 showed no evidence for a melting peak other than that corresponding to extended chain crystals, at least for $s \leqslant 4$ deg C/min. At higher heating rates, however, another low temperature peak appeared revealing the presence of folded chain crystals. Clearly, chain unfolding in this sample is much more rapid than in the previous examples, and the melting point corresponding to the once folded chain crystal (~50 °C) could not be determined unambiguously by the extrapolation procedure described above.

The behavior of F 3000 is a borderline case, since quenched specimens of the lower molecular weight fractions ($M_n < 2000$) investigated previously (7) showed only one endothermic peak corresponding to the melting of extended chain crystals. In these samples, therefore, folded chain crystals, if any, unfold too rapidly to be observed at heating rates of 32 deg C/min, or less.

Stability criterion

From the above observations a definite pattern emerges. This is shown by tab. 2, where the trend for chain unfolding during heating is compared with the calculated average crystal thickness $L = \lambda/(1+n)$. Two features are striking.

Firstly, for each of crystal types marked *O* (meaning: never observed by DSC) crystal growth rate measurements (5, 14) reveal that these species of crystal do in fact form at the growth face at high supercooling. Thus the fact that they are not observed by DSC must mean that the vast majority of chains unfold to the next lower value of n at the crystallisation temperature, or during heating at $s \leqslant 32$ deg

Tab. 2. Thermal stability of folded chain PEO crystals

Sample	n	Molecular Conformation	L (nm)	Stability
H 10000	1	⊔	31.51	S
H 10000	2	⊓⊔	21.01	S
H 10000	3	⊔⊓⊔	15.76	U
H 10000	4	⊓⊔⊓⊔	12.60	O
C 8000	1	⊔	24.53	S
C 8000	2	⊓⊔	16.35	U
C 8000	3	⊔⊓⊔	12.26	O
H 6000	1	⊔	18.87	S
H 6000	2	⊓⊔	12.58	O
H 4000	1	⊔	12.33	U
H 4000	2	⊓⊔	8.22	O
F 3000	1	⊔	8.79	U–O

Keys: S : Stable in DSC for $0.5 \leqslant s \leqslant 32$ deg C/min.
U : Unstable in DSC for $0.5 \leqslant s \leqslant 32$ deg C/min.
U–O: Unstable in DSC, only observed for $s \geqslant 8$ deg C/min.
O : Not observed by DSC with $s \leqslant 32$ deg C/min.

C/min. In all these cases, except the once folded chain F 3000, such crystals are also undetectable by small angle X-ray scattering (SAXS) at room temperature (3), implying that the large majority of chains unfold during crystal growth at T_c (5).

Secondly, it is significant that H 10000 and C 8000 both show chain unfolding during heating (classified as unstable crystals (U) in tab. 2) within a similar range of rate (determined by s) for crystals of nearly equal thickness (in both cases $L \simeq 16$ nm). Once folded chain H 4000 and F 3000 crystals do not fit this scheme since they are considerably thinner ($L = 12.3$ and 8.8 nm, respectively) but nevertheless chain unfold at comparable rates. Indeed other crystals of similar thickness, but involving values of n *larger than one*, appear to unfold to the next lower value of n during crystal growth rather than during heating and cannot be observed by DSC or SAXS, as mentioned above. Is the cause of this extra stability the fact that $n = 1$ which involves a higher surface concentration of chain ends and the possibility of pairing of lamellae (15) in interfaces containing predominantly OH end groups? A tentative answer to this question will be given later.

Isothermal thickening during crystallisation

Even in the case of stable crystals (tab. 2) multiple melting peaks often occur showing the presence of crystalline lamellae of different discrete thicknesses. This must be interpreted in terms of partial thickening during the isothermal growth process. So far however this phenomenon has only been observed directly in isolated single crystals, surrounded by the melt. These grow by deposition of n-times folded chains (determined by chain length and T_c) but their interior thickens stepwise by reducing the number of folds to $n-1$ and subsequently to $n-2$ and so on, until $n = 0$ (5, 13, 14).

The kinetics of chain unfolding has been investigated by direct observation of melt grown PEO single crystals under the optical microscope. It has been shown in particular that the thickening process involves a nucleation act, characterised by an incubation time τ and subsequently the lateral expansion of the thickened crystal portion, characterised by a growth rate G_ϕ. Both of these processes involve the diffusion of chains from the melt into the crystal lattice along the c axis. Nevertheless, τ^{-1} and G_ϕ both decrease with increasing T_c, as does the overall rate of thickening. On the other hand the magnitude of these parameters, at constant degree of supercooling, strongly decreases with increasing lamellar thickness. For crystals listed in tab. 2, the range of variation of τ and G_ϕ covers more than six orders of magnitude. Finally, the nucleation and growth processes are both arrested when the melt surrounding the crystal is depleted (5, 13, 14).

To follow the course of lamellar thickening in whole specimens, DSC experiments were carried out as part of the present study. The example chosen for detailed investigation concerns the transition from $n = 1$ to $n = 0$ of H 6000 crystals, since the corresponding melting peaks are well separated in temperature for easy resolution and yet once folded chain crystals are stable during heating at $s \geqslant 0.5$ deg C/min (cf. tab. 2).

The procedure adopted was as described above for this fraction except that the isothermal crystallisation was now interrupted by quenching the specimens at different values of t_c, covering a wide range. The experiments were carried out at three temperatures (55.5, 57.2 and 58.5 °C) at which the crystals grow in the once folded chain form relatively slowly (5) and subsequently unfold. For each set of crystallisation conditions (T_c and t_c) several specimens were melted in the DSC at different heating rates.

T_m values were determined from the peak temperatures observed at $s = 0.5$ deg C/min. The partial enthalpy change ΔH_0 correspond-

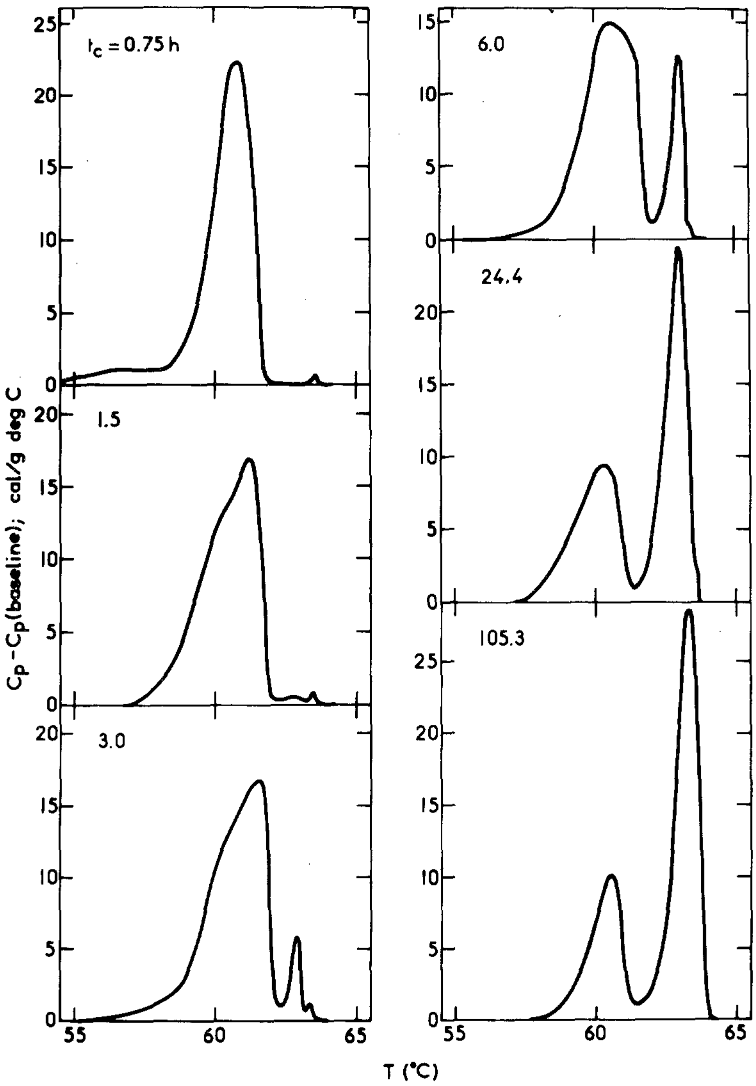

Fig. 5. Melting endotherms obtained at $s = 0.5$ deg C/min for PEO H 6000, crystallised at $T_c = 57.20$ °C for different times t_c and quenched, showing stepwise isothermal thickening with twin melting peaks of extended and once folded chains

ing to the melting of the extended chain ($n = 0$) portion of the specimens was found to be independent of s. The results given here are averages over at least two values of s.

To illustrate the melting behaviour of these specimens a typical sequence of melting endotherms, at $s = 0.5$ deg C/min is shown in fig. 5 for increasing t_c at $T_c = 57.2$ °C. The characteristic parameters T_m and ΔH_0 of these endotherms represented in figs. 6 and 7 will be discussed separately.

Melting temperatures

A surprising fact emerged immediately when specimens were quenched after relatively short crystallisation times. Instead of one, *two* melting peaks appeared corresponding to extended chain crystals, differing by 0.4 – 0.9 deg C. The small higher temperature peak appeared first, corresponding to about one percent, or less, of the whole specimen. This peak was soon swamped by the second, lower temperature peak (fig. 5). In the T_m vs log t_c plot (fig. 6) distinction is made between these two melting temperatures of extended chain crystals. It is likely that the initial, higher temperature peak ($T_m \simeq 63.5$ °C) corresponds to the extended chain seed crystals, due to incomplete melting at T_s (62.40 °C in these experiments) prior to crystallisation. This suggests that the seed crystals left at T_s are about 10 per cent thicker than the average thickness of extended chain crystals of the whole sample.

Furthermore the low temperature peak corresponding to the once folded chain crystals is also composed by two overlapping peaks, separated by about 1 °C (fig. 5). Paradoxically the one obtained at low values of t_c, characterising the crystalline material obtained during quenching, appears at a higher temperature ($\sim$61.5 °C) than that belonging to the once folded chain crystals grown isothermally at T_c. This finding is nevertheless consistant with the observations made on individual crystals which have shown (13) that once folded chain crystals grown at high supercooling melt at slightly higher temperature than those obtained at low supercooling.

It is likely that all these peculiarities result from some specific fractionation process caused by crystallisation and partial melting, and/or from the modification of the disordered surface layer with t_c, due to partial chain unfolding (at $t_c < \tau$) involving an increase of cilia length, discussed previously (cf. fig. 7 in Ref. 13).

Fig. 6 shows that for $t_c > 6$ h, the T_m values of extended chain crystals of H 6000 do not vary significantly with crystallisation time and temperature. Even the average T_m value of the two peaks observed at $t_c < 6$ h corresponds closely to that measured at longer times. For once folded chain crystals, however, T_m slightly decreases with increasing t_c and T_c, consistently with the effect shown in fig. 5. Nevertheless, its overall average value (60.9 °C) exceeds only by 0.2 °C that of mature

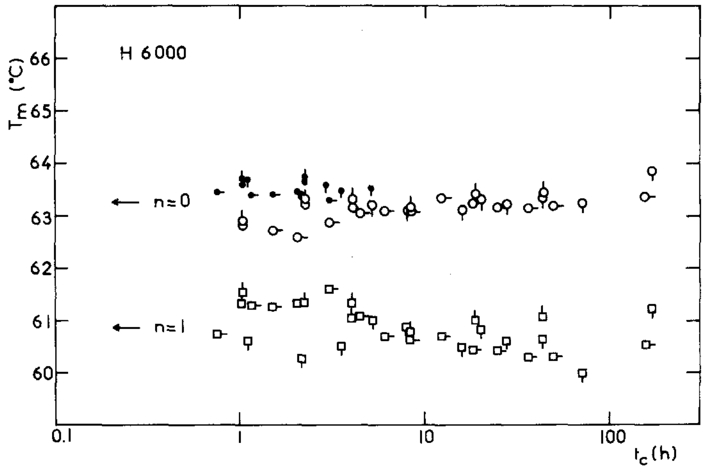

Fig. 6. Variation of melting points vs t_c of PEO H 6000 during crystal growth in once folded chain form at $T_c = 55.50$ (pip up), 57.20 (pip horizontal) and 58.50 (pip down) °C

crystals of this type obtained isothermally in a wide range of T_c (cf. tab. 3).

Kinetics of chain extension

The overall increase with log t_c of the enthalpy ΔH_0, corresponding to the extended chain portion of the crystals, is shown in fig. 7. These curves exhibit a sigmoidal pattern reminiscent of crystallisation isotherms (9, 17). By shifting along the time axis, however, they do not superpose even if normalised to the limiting values of ΔH_0 obtained at long times. Both initial and average rates of chain extension *increase* with decreasing T_c, consistent with previous results on isolated single crystals (5, 14). The limiting values of ΔH_0, however, *decrease* with T_c, presumably because the melt required for the thickening to occur is exhausted sooner. In fact, the growth rate G of once folded chain crystals increases much faster with decreasing T_c than does the rate G_ϕ of chain unfolding; the ratio G/G_ϕ varies from about 10 to 25 when T_c decreases from 58.5 to 55.5 °C (5,13). It should be noted that the final level of ΔH_0, thus the limiting proportion of extended chains, also varies with the initial concentration of extended chain seeds which in these experiments was maintained approximately constant by precise control of T_s.

Ideally the kinetics of thickening should involve an Avrami exponent (17) of 2 (two dimensional growth of the thickened portions around the seeds). Actually however this exponent is smaller than 2 at $T_c = 55.5$ and 57.2 °C, whereas it reaches 2.3 at 58.5 °C. This discrepancy indicates that at the lower values of T_c the thickening process is slowed down by the depletion of the melt much before the lamellae impinge, whereas at $T_c = 58.5$ °C, in addition to the lateral expansion, the nucleation process of thickening becomes operative (5, 13), involving ideally an Avrami exponent of 3. There is also some indication that chain unfolding is still operative (at a decreased rate) during the so called secondary crystallisation process (9). The kinetics of chain unfolding during isothermal crystallisation of a whole sample are clearly complicated since they depend on the details of the threedimensional texture built up by the space-filling lamellae.

Dependence of melting points on molecular parameters

Specimens of the samples listed in tab. 1, were fully crystallised at various temperatures between 25 and 60 °C. As mentioned above, T_m values were determined from the peak temperatures measured at $s = 0.5$ deg C/min, whereas the overall enthalpy of melting, ΔH, was derived from the total area of peaks obtained at $s = 2$ deg C/min, for the sake of greater precision. Results are collected in figs. 8–11 where each point represents an average of

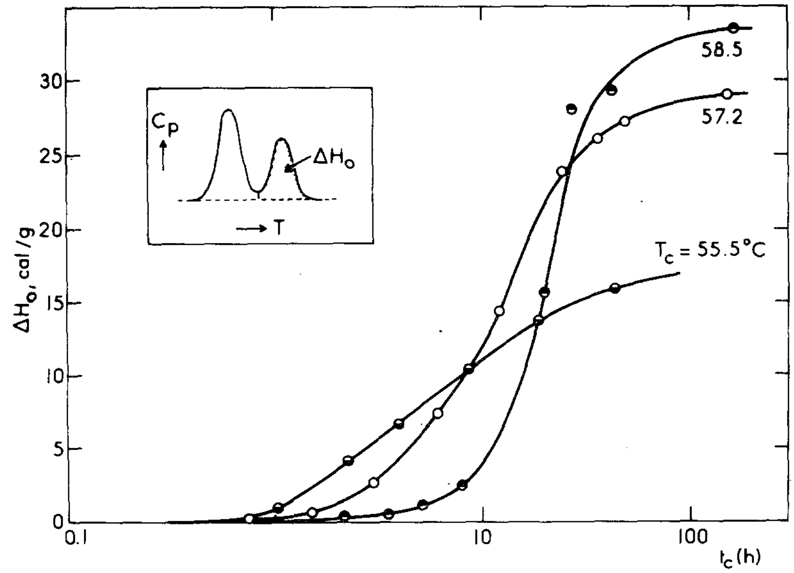

Fig. 7. Crystallisation time dependence of the fractional enthalpy of melting ΔH_0 of extended chain crystal portions, per g of whole sample

at least two measurements on different specimens.

Clearly, the melting temperatures are essentially independent of T_c, as pointed out by other authors (16). This invariance is to be expected for extended chain crystals, but appears unusual for folded chain crystals, whose melting points generally increase monotonically with T_c in parallel with their thicknesses (18). Consequently, the invariance of T_m for folded chain PEO crystals must reflect the invariance of their thickness with respect to T_c as already shown by SAXS (1–3).

The occurrence of several distinct melting temperatures for a single specimen thus indicates the coexistence of crystalline lamellae with

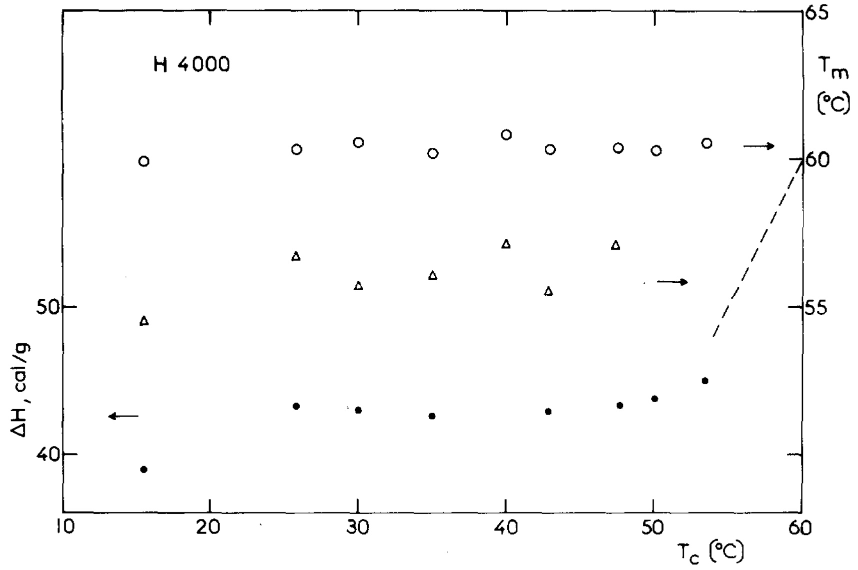

Fig. 8. T_m and ΔH measurements for PEO H 4000 isothermally crystallised at various temperatures T_c. o: extended, Δ: once folded chain crystals. The arrow at the lowest T_m indicates the melting point observed by the extrapolation procedure for once folded chain crystals. Dashed line: $T_m = T_c$

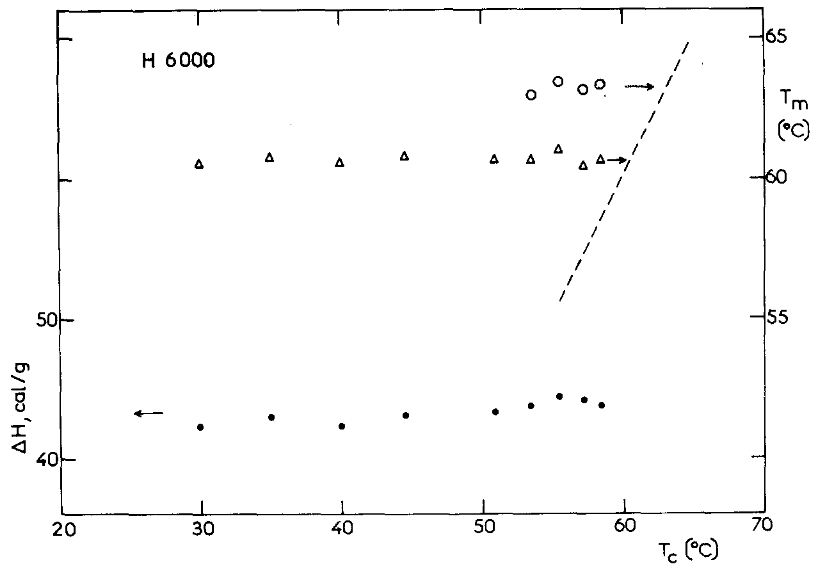

Fig. 9. T_m and ΔH measurements for PEO H 6000 isothermally crystallised at various temperatures T_c. o: extended, Δ: once folded chain crystals. Dashed line: $T_m = T_c$

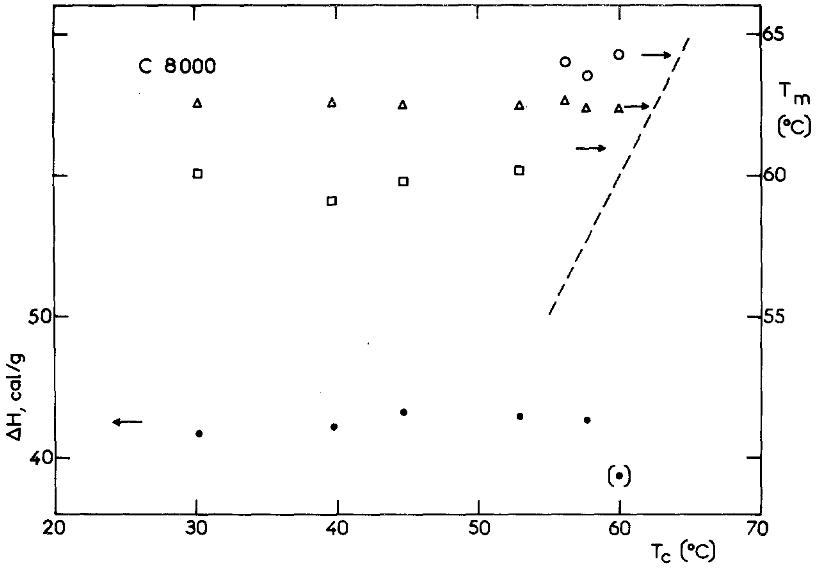

Fig. 10. T_m and ΔH measurements for PEO C 8000 isothermally crystallised at various temperatures T_c. o: extended, Δ: once folded and □ twice folded chain crystals. The arrow at the lowest T_m indicates the melting point obtained by the extrapolation procedure for twice folded chain crystals. Dashed line: $T_m = T_c$

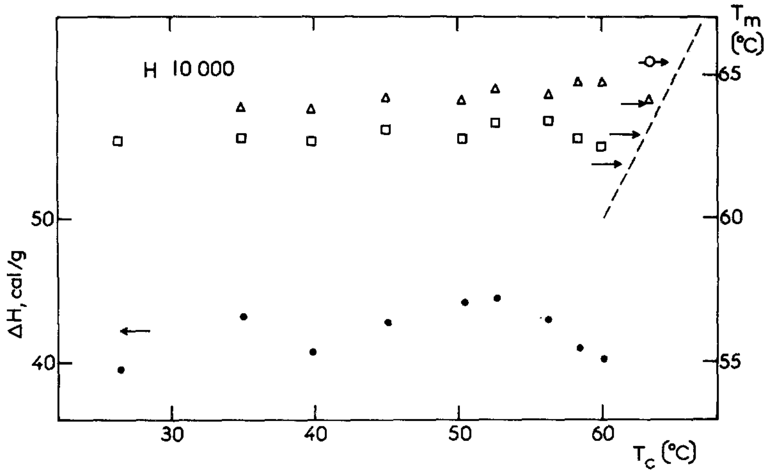

Fig. 11. T_m and ΔH measurements for PEO H 10000 isothermally crystallised at various temperatures T_c. o: extended, Δ: once folded, □ twice folded chain crystals. The arrow at the lowest T_m indicates the melting point obtained by the extrapolation procedure (cf. fig. 4) for three-times folded chain crystals. Dashed line: $T_m = T_c$

different thicknesses determined by the number n of folds per molecule. The proportion of thicker lamellae (smaller n) was always found to increase with T_c and t_c, as shown above for H 6000 (figs. 5 and 7), as a consequence of chain unfolding during isothermal crystal growth (5). For unstable crystals this proportion was further increased by subsequent chain unfolding during heating in the DSC, as demonstrated above for H 4000 (fig. 3).

On the basis of previous work by SAXS (3) and microscopy (5, 14) the various melting peaks were assigned to either extended chain crystals ($n = 0$) or to the various types of folded chain crystals characterised by integer values of $n \geqslant 1$. Results obtained for extended chain crystals have been discussed before (7). They are also included in figs. 8–11 for the sake of completeness, with the addition of a more recent determination of $T_m = 65.4$ °C for extended chain crystals of H 10000.

a) The scatter in T_m for *stable crystals* (tab. 2) was generally within experimental error and average values (indicated by arrows in figs. 8–11) will be used in the analysis which follows. One exception however should be mentioned. In the case of H 10000 once folded chain crystals, T_m increased with T_c for $T_c \geqslant 52.6$ °C owing to the onset of fractionation. Therefore the average T_m for these crystals was calculated using only data for $T_c < 52.6$ °C which probably best represents the average chain length of the whole sample.

b) For *unstable crystals* (tab. 2) showing larger scatter in T_m, the adopted melting points were determined by the extrapolation procedure described above (cf. fig. 4). As expected, these values, indicated by arrows in figs. 8, 10 and 11, are smaller than those derived from T_p, at $s = 0.5$ deg C/min, plotted in figs. 8–11. In this respect the twice folded C 8000 crystals showed an opposite behaviour (cf. fig. 10), the origin of which, presumably due to some fractionation during heating, is not clear at present.

The different T_m values so obtained are summarised in tab. 3. They are quoted as $T_m(n, p)$ in order to emphasise their separate dependence on the degree of polymerisation p and the number of folds per molecule n, both determining the crystal thickness.

Tab. 3. Melting point $T_m(n, p)$ values of extended ($n = 0$) and folded chain PEO crystals of the various samples studied

Sample	p	n	$T_m(n, p)$(°C)
H 10000	226.6	0	65.4
H 10000	226.6	1	64.0
H 10000	226.6	2	62.9
H 10000	226.6	3	61.8
C 8000	176.4	0	64.3
C 8000	176.4	1	62.5
C 8000	176.4	2	61.0
H 6000	135.7	0	63.3
H 6000	135.7	1	60.7
H 4000	88.6	0	60.4
H 4000	88.6	1	55.9
F 3000	63.2	0	57.6
H 2000	42.9	0	52.7

The overall enthalpy of melting ΔH is also plotted against T_c for each sample in figs. 8–11. Although there is some scatter, ΔH appears to be independent of T_c. On the other hand the average values, indicated by arrows, do not show any significant molecular weight dependence, the overall mean value being 42.7 cal/g. Comparing this value to that obtained for a perfect crystal of infinite dimensions (cf. eq. [10] in Ref. 7), *i.e.* 47.0 cal/g, the average crystallinity of these samples amounts to about 91 per cent.

Theoretical

We adopt here the same method of analysis as was recently applied to the melting of extended chain PEO crystals (7), by considering the folded chain crystal model shown in fig. 12. For simplicity this figure shows the fold planes parallel to the prism faces. This

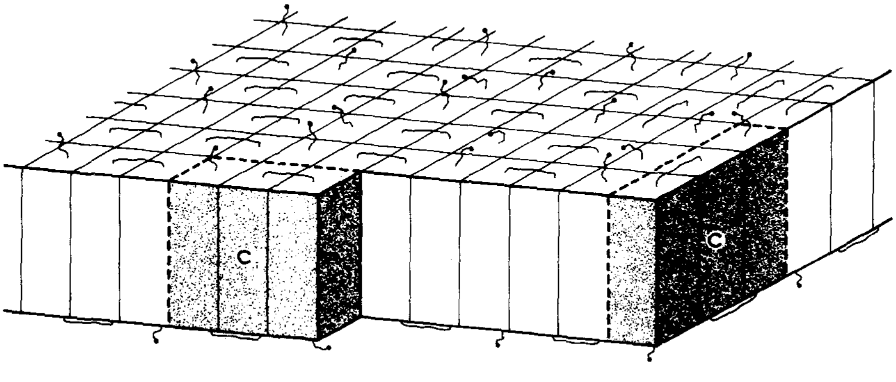

Fig. 12. Folded chain polymer crystal model. (The length along the chain axis is reduced by a factor of about 10 with respect to the interchain spacing)

need not be so. In fact, the formal treatment used here is more generally applicable, requiring only that all crystal planes parallel to the melting faces be alike.

Assuming, as before, that T_m is the temperature at which the chemical potential μ_c of molecules occupying crystal sites of type c becomes equal to that of molecules in the liquid state, μ_l, one can write:

$$\Delta\mu(T_m) \equiv \mu_l(T_m) - \mu_c(T_m) = 0. \qquad [1]$$

Let the total surface *Gibbs'* free energy contribution of one n-times folded molecule in the crystal be $\sum(n, T)$, which in general depends on both n and T. If all folds are identical one can immediately state:

$$\sum(n, T) = 2\sigma_{e,e}(n, T) + 2n\sigma_{e,f}(n, T) \qquad [2]$$

where $\sigma_{e,e}$ and $2\sigma_{e,f}$ are the respective surface free energy contributions of one chain end and one chain fold.

It was found before (7) that for extended chain crystals of PEO a structure consisting of closely stacked lamellar crystals had to be invoked to satisfactorily explain the molecular weight dependence of $T_m(0, p)$ over a wide range of M_n. This corresponds to assuming that the entropy of chain ends at the crystal surface is independent of molecular weight and leads to the theory of *Flory* and *Vrij* (19).

The same assumption is also reasonable for folded chain crystals of PEO, in view of the close regular stacking of crystal lamellae indicated by SAXS (2). For n-times folded chain crystals of a PEO fraction containing p monomer units per molecule this leads to:

$$\Delta\mu(T) = p\,[\Delta H^*(T) - T\Delta S^*(T)] - \sum(n, T) - RT\,ln\,pC \qquad [3]$$

where ΔH^* and ΔS^* are the molar enthalpy and entropy of melting per monomer unit in an extended chain crystal of infinite dimensions, melting at

$$T_m(\infty) = \Delta H^*/\Delta S^*, \qquad [4]$$

R is the gas constant and C a constant related to the flexibility of PEO chains in the melt (19). Since in the present work the range of T_m values, including $T_m(\infty)$, covers only 14 deg C, variations of $\Delta H^*(T)$ and $\Delta S^*(T)$ with T would amount to less than ca. 1 % (7) and will be neglected.

Eq. [3] may be substituted into eq. [1] and rearranged to give an expression for $\sum$ at the appropriate melting point $T_m(n, p)$:

$$\begin{aligned}\textstyle\sum^+(n, T_m) \equiv \sum(n, T_m) + RT_m\,ln\,C \\ = p\frac{\Delta H^*}{T_m(\infty)}\,[T_m(\infty) - T_m] \\ - RT_m\,ln\,p.\end{aligned} \qquad [5]$$

The additional parameter $\sum^+(n, T_m)$ has been introduced for convenience, since in the absence of an independent determination of C, the surface free energy $\sum(n, T)$ cannot be separated from the essentially constant term involving C.

Using the recently established values (7) of $T_m(\infty) = 68.9$ °C and $\Delta H^* = 2.07$ Kcal/mole, eq. [5] was applied to the present $T_m(n, p)$ measurements (tab. 3) to yield $\sum^+(n, T_m)$. The results are shown in fig. 13 as a function of $T_m(n, p)$, temperatures at which they were determined, together with $\sum^+(0, T) = 2\sigma_{e,e} + RT\,ln\,C$, derived from previous work on extended chain crystals (see Appendix 1). The rectangles around the data points indicate the possible errors due to the ± 0.2 deg C uncertainty in the values of T_m. There is clearly some evidence for temperature dependence of $\sum^+$. Postulating that in the temperature range of interest $\sum^+(n, T)$ is a linear function of T as established previously (7) for $\sum^+(0, T)$, and assuming that its temperature coefficient

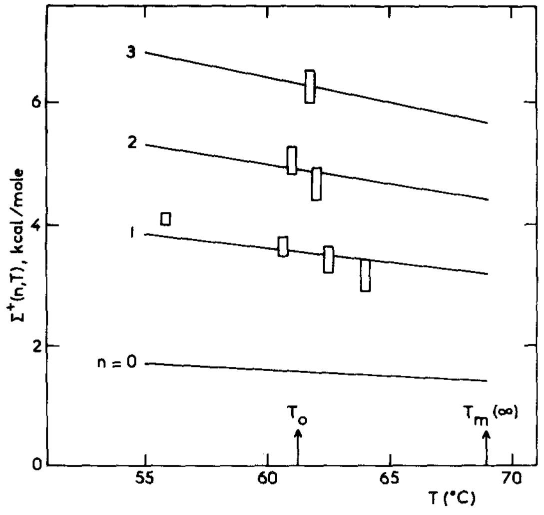

Fig. 13. Total surface free energy $\sum^+$ of n-times folded chain crystals as a function of their melting temperature

$$\frac{1}{\sum^{+}(n,\,T_o)} \cdot \frac{d\sum^{+}(n,\,T)}{dT} = -\,\alpha \qquad [6]$$

is independent of n, one can write, as a first approximation:

$$\sum^{+}(n,\,T) = \sum^{+}(n,\,T_o)\,[1 - \alpha(T - T_o)] \qquad [7]$$

where T_0 is a reference temperature which will be chosen here as the mean $T_m(n,\,p)$ value, equal to 61.2 °C. Applying eq. [7] to $\sum^{+}(0,\,T)$, known from previous work (7), yields (see Appendix 1)

$$\alpha = 1.29 \times 10^{-2}\,(\text{deg K})^{-1}. \qquad [8]$$

The straight lines in fig. 13 show the temperature dependence of $\sum^{+}(n,\,T)$ as derived from eqs. [7] and [8] for $n = 0, 1, 2$ and 3, by reducing the values of $\sum^{+}(n,\,T_m)$ to T_o and averaging. There is reasonable agreement with the measured temperature dependence, with some evidence that α is in fact greater for $n = 1$ than for $n = 0$. This is a barely significant effect however and no further correction was attempted.

Surface free energies

The dependence of $\sum^{+}$ on chain folding becomes clear when $\sum^{+}(n,\,T_o)$ is plotted against n, as shown in fig. 14. Two features are noteworthy:

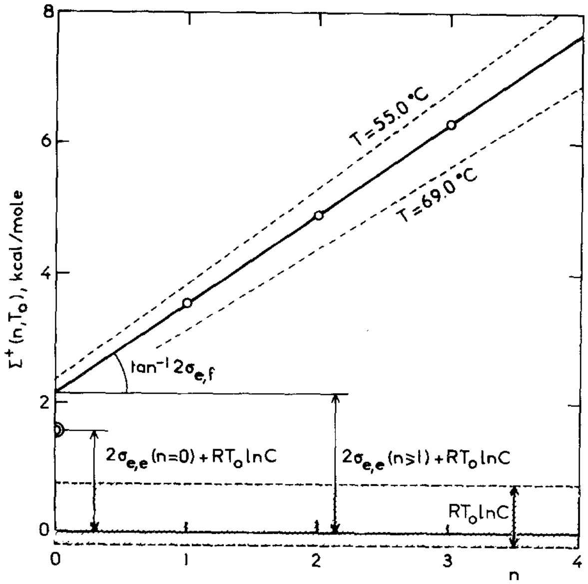

Fig. 14. Total surface free energy $\sum^{+}$ of extended and folded chain crystals as a function of n, reduced to the reference temperature $T_o = 61.2$ °C. (Dashed lines: the same at 55.0 and 69.0 °C). Shaded area shows the uncertainty in the $RT_o \ln C$ term, assuming $3/4 < C < 3$

1) For $n \geqslant 1$, $\sum^{+}(n,\,T_o)$ follows, with excellent agreement, a linear relationship of the form

$$\sum^{+}(n \geqslant 1,\,T_o) = A(T_o) + B(T_o)n \qquad [9]$$

in which $A(T_o)$ an $B(T_o)$ are constants, the values of which depend on temperature alone. Comparing eq. [9] with eq. [2] implies that, for $n \geqslant 1$, $\sigma_{e,e}$ and $\sigma_{e,f}$ are both independent of n, with values at T_o given by:

$$\begin{aligned} A(T_o) &= 2\sigma_{e,e}(n \geqslant 1,\,T_o) + RT_o \ln C \\ &= 2.15 \text{ Kcal/mole} \end{aligned} \qquad [10]$$

and

$$\begin{aligned} B(T_o) &= 2\sigma_{e,\,f}(T_o) = 1.38 \text{ Kcal/mole} \\ &\simeq 45 \text{ erg/cm}^2\ (^*)\,. \end{aligned} \qquad [11]$$

Of course, both of these values depend slightly on T_o. This may be easily accounted for by using the data given in fig. 13. The broken lines in fig. 14 show the result obtained at 55 and 69 °C, bounding the temperature interval of interest.

2) Clearly, for $n = 0$ eq. [9] exceeds significantly the value of $\sum^{+}(0,\,T_o)$ obtained from data on extended chain crystals. The difference being (see eq. [10] and eq. [A 5] in Appendix 1):

$$\begin{aligned} &2\sigma_{e,e}(n \geqslant 1) - 2\sigma_{e,e}(n = 0) \\ &= 0.58 \text{ Kcal/mole.} \end{aligned} \qquad [12]$$

This difference represents the excess surface free energy of a pair of chain ends in a composite surface of chain folds and chain ends with respect to that of a pair of chain ends in a surface containing chain ends alone.

Discussion

Unfortunately, the actual value of $\sigma_{e,e}(n \geqslant 1,\,T_o)$ cannot be obtained since C is unknown. By assuming as before (7) that $3/4 < C < 3$, it is however possible to place $\sigma_{e,e}(n \geqslant 1,\,T_o)$ between two limiting values:

$$0.71 < \sigma_{e,e}(n \geqslant 1,\,T_o) < 1.17 \text{ Kcal/mole} \qquad [13]$$

---

[*] 1 Kcal/mole ≃ 32.5 erg/cm²; see Appendix 2.

which are comparable to, or *greater* than $\sigma_{e,f}$ (cf. eq. [11]).

From the previous study $\sigma_{e,e}(n=0, T_o)$ is known to be within (cf. eq. [16] in Ref. 7, corrected for $T=T_o$)

$$0.42 < \sigma_{e,e}(n = 0, T_o) < 0.88 \text{ Kcal/mole.} \quad [14]$$

The value of $2\sigma_{e,f}$ obtained here is low compared with those reported for most other polymers (20). There are two reasons for this:

a) the PEO chain is unusually flexible and so the free energy of a chain fold might be expected to be low, and

b) the method commonly used to obtain the surface free energy of polymer crystals should be considered with caution, as discussed below, therefore determinations of σ_e reported in the literature may be unreliable.

The present value of $\sigma_{e,f}$, however, is consistent with the low value of $\sigma\sigma_{e,f}=220$ erg^2/cm^4 derived from growth rate measurements of high molecular weight PEO crystals (5, 9, 14), where σ is the surface free energy of lateral surfaces of the PEO crystal. Indeed, assuming a reasonable value of 10 erg/cm^2 for σ (21) yields $2\sigma_{e,f}=44$ ergs/cm^2 (*viz.* 1.36 Kcal/mole) in excellent agreement with the value given in eq. [11].

The average surface free energy of an n-times folded chain crystal of PEO is given by

$$\bar{\sigma}_e(n) = \frac{\sigma_{e,e}(n) + n\sigma_{e,f}}{1+n}. \quad [15]$$

Using the values of $\sigma_{e,e}(n)$ and $\sigma_{e,f}$ derived above, $\bar{\sigma}_e(n)$ *increases* between $n=0$ and $n=1$ and then gradually *decreases* towards 0.69 Kcal/mole as n increases further. Also, as is evident in fig. 13, there is little suggestion of a systematic dependence of surface free energy on molecular weight.

Both of these results are in conflict with those of *Booth* and co-workers (22, 23), who found σ_e to *decrease* by more than 30% when n increases from 0 to 1 and to show a marked molecular weight dependence. The discrepancies arise from their choice of 76 °C for T_m (∞), a value now known to be incorrect (7).

Nature of the PEO crystal surface

A pair of PEO chain ends were shown above (eq. [12]) to have an excess free energy of 0.58 Kcal/mole in a partly chain folded surface as compared with a surface composed entirely of chain ends. This fact strongly suggests that hydrogen bonding occurs between the terminal OH groups when their concentration in the surface layer is sufficiently high. One would however expect the effect to disappear only gradually with increasing n, as the average distance between nearest chain ends increases. The results shown in fig. 14 may indeed contain such a gradual change in $\sigma_{e,e}$ which cannot be resolved above experimental scatter. They do show, however, that the major change in $\sigma_{e,e}$ occurs between $n=0$ and $n=1$.

To estimate the bonding energy involved it is necessary to separate $\sigma_{e,e}$ into enthalpic and entropic contributions. A simple and reasonable assumption consistent with the treatment above is that α, defined by eq. [6], is independent of n. The enthalpy contribution to $\sum^+(n,T)$ at T_0 is then the temperature independent part of the right hand side of eq. [7], *viz.*

$$\textstyle\sum^+(n, T_0)(1+\alpha T_0) = 5.31 \sum^+(n, T_0) \quad [16]$$

whatever the value of n.

Consequently, the excess enthalpy of a pair of chain ends in a partially folded chain ($n \geqslant 1$) surface with respect to that in an entirely extended chain surface, *i.e.* the hydrogen bonding energy in the latter, amounts to (cf. eq. [12]):

$$5.31\,[2\sigma_{e,e}(n \geqslant 1) - 2\sigma_{e,e}(n=0)] \simeq 3.1 \text{ Kcal/mole} \quad [17]$$

which is of reasonable magnitude for OH pairing.

In extended chain crystals the excess surface enthalpy of one chain end ($\Delta H_e/2$) with respect to the enthalpy of the crystal amounts to 4.18 Kcal/mole (see eq. [10] in Ref. 7). It is reasonable to assume that the enthalpy of a monomer unit in the disordered surface layer equals that of a monomer unit in the melt, if due allowance is made for the presence of hydrogen bonding between chain ends in the former case. One can therefore conclude that, on average, a number $(4.18+1.55)/\Delta H^* \simeq 2.8$ monomer units constitutes a cilium for every chain end. Since the specific volume of the surface layer is always greater than that of the crystal, it follows that these layers have a thickness of at least $2 \times 2.8 \times l = 1.54$ nm *even when they consist entirely of chain ends* [l is the projection on the crystal c axis of one monomer unit and equals 0.278 nm (8); see Appendix 2].

Consider now a crystal surface containing chain folds. The surface free energy contribution of one chain fold was shown (cf. eq. [11]) to be 1.38 Kcal/mole. If α is again assumed independent of n, the excess enthalpy of a chain fold (with respect to that of the crystal) is 5.31 $(2\sigma_{e,f}) = 7.33$ Kcal/mole, implying that one chain fold contains, on average, $7.33/\Delta H^* \simeq$ 3.5 monomer units, *i.e.* half the number involved in the 7/2 helix repeat unit along the c axis (8). The contour length of a chain fold thus appears less than that of two cilia, which means that the folds must be sharp.

From these results a picture of the surface of PEO crystals emerges. Chain ends protrude from the crystal as cilia containing on average 2.8 monomer units. When there are no chain folds present, there is considerable hydrogen bonding between the terminal OH groups with an average bonding energy of 3.1 Kcal/mole. Chain folds occur as short loops with adjacent re-entry, since they each contain only 3.5 monomer units on average.

It should be pointed out that these estimated lengths for cilia and chain folds are only approximate, as they rely on two crucial assumptions: a) that α is a constant independent of n and (b) that the enthalpy of a monomer unit in the disordered surface layer equals its corresponding value in the melt. Nevertheless, for crystals about 15 nm thick, these estimates lead to an amorphous content of the order of 10 per cent which is consistent with the average crystallinity of the samples investigated, as derived above from ΔH data (figs. 8–11) and from unpublished dilatometric measurements.

Wider implications for the melting of polymer crystals

A method commonly used for determining $T_m(\infty)$ and σ_e for polymer crystals is to assume a linear relation between T_m and $1/L$

$$T_m(1/L) = T_m(\infty)\left(1 - \frac{2\sigma_e l}{L\cdot\Delta H^*}\right) \qquad [18]$$

where l is included because σ_e and ΔH^* are expressed in molar units. Eq. [18] can be shown to apply to the melting of a polymer crystal of thickness L and *infinite* molecular weight (20). For polymers of finite chain length, however, great care must be exercised in its application. On the basis of the present work one can examine in detail the limitations of this equation.

By substituting eq. [7] into eq. [5] and rearranging one can derive an accurate expression for $T_m(n,p)$:

$$T_m(n,p) = \frac{T_m(\infty)\left[1 - \dfrac{\sum^+(n,T_0)\,(1+\alpha T_0)}{p\cdot\Delta H^*}\right]}{1 + \dfrac{\ln p}{p}\cdot\dfrac{RT_m(\infty)}{\Delta H^*} - \dfrac{T_m(\infty)\cdot\sum^+(n,T_0)\cdot\alpha}{p\cdot\Delta H^*}} \qquad [19]$$

The corresponding crystal thickness is given by:

$$L(n,p) = lp/(1+n)\,. \qquad [20]$$

Taking the values of $\sigma_{e,e}(n=0)$, $\sigma_{e,e}(n \geqslant 1)$ and $\sigma_{e,f}$ derived above for temperature T_0 to give $\sum^+(n,T_0)$ *via* eq. [2], eqs. [19] and [20] were used to compute $T_m(n,p)$ as a function of $1/L$ for different values of n. The result is shown by the curves in fig. 15, for $n = 0$, 1, 2, 3, 10 and ∞, together with the measured values of T_m listed in tab. 3. Clearly, *there is no unique relation between* T_m *and* $1/L$, since both of them depend differently on two independent molecular parameters, p and n. Note also that for fractional values of n eq. [19] is not applicable, since it was derived by assuming all the chain ends to be rejected onto crystal surface layers (cf. eq. [2]).

An additional problem arises from the instability of folded chain polymer crystals which thicken with an increasing rate as their thickness decreases (see above). For each value of $n \geqslant 1$, one can thus define a narrow thickness range around a critical value L^* such that crystals with $L < L^*$ thicken appreciably during heating (at a given rate s) to a thickness $L > L^*$. For this reason the $T_m(1/L)$ curves only have practical meaning for $L > L^*$. In fig. 15 therefore the curves for $n \geqslant 1$ have each been truncated at a value of L below which the thermal stability of PEO crystals vanishes, as derived from Table 2. Dashed portions indicate the uncertainty in the correct cut-off point as

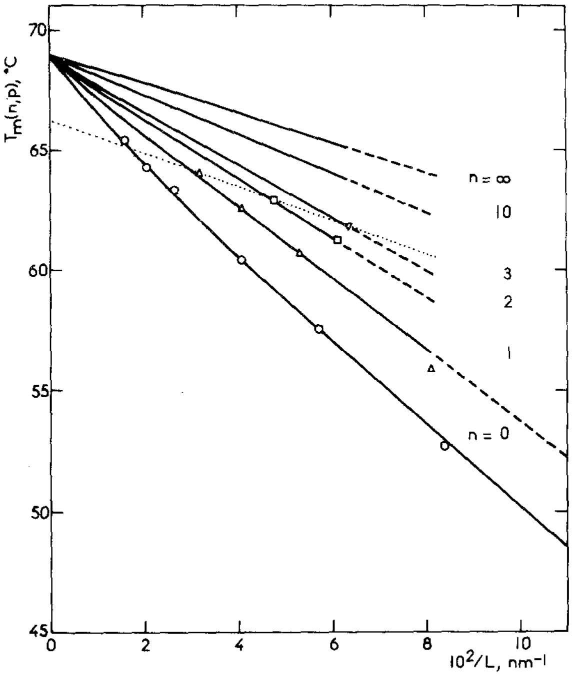

Fig. 15. Variation of T_m versus $1/L$ for different values of n, as predicted by eq. [19] (using values for $\sigma_{e,\,e}(n \geqslant 1)$ and $\sigma_{e,f}$ derived in this work and $\sigma_{e,\,e}(n=0)$ from Ref. 7), together with the experimental $T_m(n,p)$ data obtained in previous (7) and present work (tab. 3). Dashed lines indicate uncertainty in the correct cut-off points

determined in this work. Because of this limited thermal stability of folded chain polymer crystals, one cannot safely assign a T_m value to a crystal thickness measured, as usually, at room temperature, unless $L > L^*$. At present it is not known whether L^* is as well defined for other polymers as it is for OH terminated, low molecular weight fractions of PEO. If so, its value is probably greater than 10 nm when chain unfolding occurs gradually rather than stepwise.

The second point to be emphasized is the large contribution to $T_m(1/L)$ of the *ln p/p* term in eq. [19] which is neglected in eq. [18]. This term arises from assuming the environment of chain ends in the crystal surface layer to be composed solely of other chain ends or chain folds, protruding from the same lamella and/or adjacent lamellae (7, 19). This seems a reasonable general assumption, given the well known regular stacking of lamellar polymer crystals. Three cases should be considered.

a) For a given value of n, the *ln p/p* term has two effects on fig. 15. *First*, the $T_m(1/L)$ curves deviate from linearity, especially as $1/L$ approaches zero and when n is small. The contribution of this upward curvature to the value of $T_m(\infty)$ is small as compared to that obtained by linear extrapolation of the T_m data to $(1/L)=0$, suggested by eq. [18]. The latter thus yields an underestimate of $T_m(\infty)$ by about 1 °C or less. *Second*, the negative slope of the curves strongly decreases in magnitude with increasing n; according to [18] this implies a large *decrease* in σ_e with increasing n. In the present analysis however there is no evidence for this; indeed, it has been shown that σ_e *increases* appreciably when n varies from 0 to 1. Simple application of eq. [18] to the extended chain data shown in fig. 15 would result in an apparent value for $\sigma_{e,\,e}(n=0)$ of 2.0 Kcal/mole, which is at least a factor of 2 too large (cf. eq. [14]).

b) Instead of n, p is maintained constant, eq. [18] will again lead to an underestimate of $T_m(\infty)$ even for crystals involving large values of n, provided that the molecular weight is finite. Consider an experiment in which a given polymer fraction is subjected to different thermal treatments to achieve different values of L and the corresponding melting points T_m are measured in order to determine $T_m(\infty)$ and σ_e using eq. [18]. For simplicity let $n \gg 1$ and let the range of T_m involved be small enough for the temperature variation of σ_e to be negligible, hence:

$$\left.\begin{aligned} \Sigma^+ &\simeq 2\sigma_{e,f}\cdot n \\ p &\simeq nL/l \\ \alpha &= 0\,. \end{aligned}\right\} \qquad [21]$$

Substituting in eq. [19] gives, as a first approximation:

$$T_m \simeq T_m(\infty)\left(1-\frac{2\sigma_{e,f}l}{L\cdot\Delta H^*}\right)-\frac{RT_m^2(\infty)}{\Delta H^*}\cdot\frac{\ln p}{p}\,. \qquad [22]$$

Eq. [22] shows a linear relationship between T_m and $1/L$ in *apparent* agreement with eq. [18], with a slope yielding the correct value of $\sigma_{e,f}$. The ordinate intercept at $(1/L)=0$, however, would clearly be less than the value of $T_m(\infty)$; the difference increases with decreasing p. This discrepancy has already been pointed out by *Broadhurst* (24). To obtain the correct value of $T_m(\infty)$ it is necessary to add to the ordinate intercept the *ln p/p* term of eq. [22].

The dotted line in fig. 15 drawn through the experimental values of $T_m(n \geqslant 1, p)$ for sample H 10000 clearly emphasizes the discrepancies arising from the use of eq. [18].

c) If melting point depression with decreasing lamellar thickness is investigated on several fractions, with varying n and p, there is an additional error in eq. [18] besides omission of the *ln p/p* term, since L now depends on two independent molecular parameters n and p and σ_e varies with n.

A vivid illustration of this statement is provided by the present results, collected in tab. 3 and illustrated in fig. 15. The following pairs of crystal types have closely similar thicknesses: extended chain H 2000 and once folded H 4000 ($L \simeq 12$ nm), extended chain F 3000 and once folded H 6000 ($L \simeq 18$ nm), extended chain H 4000 and once folded C 8000 ($L \simeq 24.5$ nm). In each case, however, the melting point of extended chain crystals lies 2 to 3 deg C *below* that of once folded chain crystals of equal thickness, although the average surface free energy $\bar{\sigma}_e$ (eq. [15]) *increases* when n increases from 0 to 1 (see above).

Finally, another approximation in eq. [18] is made by neglecting the temperature dependence of σ_e, which from the present work amounts to a decrease of 1.3% per deg C. Its effect in figure 15 is to give all the curves a slight downward trend with increasing $1/L$ (cf. fig. 6 in Ref. 7), thus to increase the *apparent* values of σ_e and $T_m(\infty)$.

Conclusions

Chain folding is one of the major issues of polymer science. It is for this reason that the crystal surface free energy σ_e is of such great interest. The present work, however, has shown the usual method of determining σ_e, via eq. [18], to lack general validity, since it applies accurately only to polymers of infinite molecular weight. An added problem is the inherent thermal instability of folded chain polymer crystals, which means that the crystal thickness L entering in eq. [18] may increase during heating to the melting point.

Both of these problems have been overcome here by (a) developing a self-consistent theoretical analysis to allow for the effect of finite molecular weight and (b) studying low molecular weight fractions of PEO, for which even chain folded crystals have unusual thermal stability.

Crystal thickening has been shown to occur in whole samples in a manner analogous to crystallisation, consistent with microscopic observations of thickening of isolated crystals grown from the melt. Isothermal thickening at the crystallisation temperature takes place at a rate which increases with decreasing temperature and with decreasing crystal thickness. The final degree of transformation achieved in a whole sample at T_c is probably determined merely by exhaustion of the melt. Thickening during heating at constant rate or annealing also occurs faster with decreasing crystal thickness. These two effects place a lower limit L^* on the crystal thickness for which a corresponding T_m may be determined. The present work shows that for PEO, $12.3 > L^* > 8.8$ nm for $n = 1$ and $16.4 > L^* > 12.3$ nm for $n \geqslant 1$ (cf. tab. 2).

Applying the correct analysis to T_m data for PEO crystals yields values for the surface free energy (a) of chain ends in an environment of only chain ends $\sigma_{e,\,e}(n = 0)$, (b) of chain ends in an environment of chain ends and chain folds $\sigma_{e,\,e}(n \geqslant 1)$ and (c) of chain folds $\sigma_{e,\,f}$. The different values of the characteristic parameters derived are listed in Appendix 2.

The results suggest there is considerable hydrogen bonding between OH end groups, with a bonding energy of 3.1 Kcal/mole, when the surface contains only chain ends. This hydrogen bonding is essentially destroyed by chain folding. The cilia associated with chain ends are estimated to each contain ca. 2.8 monomer units. Chain folds are similarly estimated to each contain ca. 3.5 monomer units. Chain folding in PEO crystals mus therefore be fairly regular with adjacent re-entry.

Using the same analysis, it is possible to critically examine the usual method of determining $T_m(\infty)$ and σ_e for polymer crystals from T_m and L measurements. Such experiments may be performed in one of two ways:

a) If L is varied by changing molecular weight at constant n, the method greatly overestimates σ_e at low values of n. This error disappears as n approaches infinity.

b) If on the other hand L is varied by changing n for a polymer fraction of given molecular weight, the chief error is an underestimate of $T_m(\infty)$. This error disappears again as the molecular weight tends to infinity.

Work is in progress to extend the present analysis to the melting behaviour of blended PEO fractions.

Appendix 1

According to the present definition of $\sum^+(n, T)$ given by eq. [5] the corresponding surface free energy in terms of the notations used in Ref. 7, may be written as

$$\begin{aligned}\textstyle\sum^+(0, T) &= 2\sigma_{e,e}(0) + R\,T\,ln\,C\\ &= \Delta H_e - T(\Delta S_e - R\,ln\,C) \quad [\mathrm{A\ 1}]\end{aligned}$$

where $\Delta H_e/2$ and $\Delta S_e/2$, the respective enthalpic and entropic contributions (per mole of chain end in extended chain crystals) to $\sigma_{e,e}(0)$, are assumed to be temperature independent.

Thus, at $T = T_o$

$$\textstyle\sum^+(0, T_o) = \Delta H_e - T_o(\Delta S_e - R\,ln\,C). \quad [\mathrm{A\ 2}]$$

Eliminating ΔH_e from eqs. [A 1] and [A 2] yields

$$\begin{aligned}\textstyle\sum^+(0, T) &= \textstyle\sum^+(0, T_o)\\ &\quad \left[1 - \frac{\Delta S_e - R\,ln\,C}{\sum^+(0, T_o)}(T - T_o)\right]\\ &= \textstyle\sum^+(0, T_o)\,[1 - \alpha(T - T_o)] \quad [\mathrm{A\ 3}]\end{aligned}$$

in which

$$\begin{aligned}\alpha &= -\frac{1}{\sum^+(0, T_o)} \cdot \frac{d\sum^+(0, T)}{dT}\\ &= \frac{\Delta S_e - R\,ln\,C}{\sum^+(0, T_o)}. \quad [\mathrm{A\ 4}]\end{aligned}$$

By substituting the previously derived values of

$\Delta H_e/2 = 4.18$ Kcal/mole (eq. [10] in Ref. 7)

and

$\Delta S_e - R\,ln\,C = 20.3$ cal/deg. mole (eq. [12] in Ref. 7)

into eqs. [A 2] and [A 4] one obtains at $T = T_o = 334.4$ °K

$$\begin{aligned}\textstyle\sum^+(0, T_o) &= 2\sigma_{e,e}(0) + R\,T_o\,ln\,C\\ &= 1.57 \text{ Kcal/mole} \quad [\mathrm{A\ 5}]\end{aligned}$$

and

$$\alpha = 1.29\ 10^{-2}\ (\text{deg K})^{-1} \quad [\mathrm{A\ 6}]$$

which are the values adopted for calculating the temperature dependence of $\sum^+(n, T)$ given by eq. [7] and represented in fig. 13 by the straight lines for $n = 0$, 1, 2 and 3.

Appendix 2

Thermodynamic parameters controlling the melting behaviour of extended and folded chain PEO crystals derived from previous (7) and present work.

The following literature data has been used:

a) Crystal lattice parameters (8):
$a^* = a \sin \beta = 0.656$ nm,
$b = 1.304$ nm and $c = 1.948$ nm.

- Cross section of the PEO chain, A_o:
  $A_o = a^*\,b/4 = 0.214$ nm^2.
- Molar mass per unit length v, along the c axis:
  $v = 7 \times 44.02/c = 158.2$ g/nm.
- Projection of the length l of one monomer unit on the crystal c axis:
  $l = c/7 = 0.2783$ nm.

b) Specific heat increment ΔC_p on melting, per monomer unit, derived from data of *Beaumont* et al. (25)

$$\begin{aligned}\Delta C_p &= 2.07 \text{ cal/mole. deg C}\\ &\simeq 0.047 \text{ cal/g. deg C.}\end{aligned}$$

Bulk parameters

Melting point $T_m(\infty)$ of PEO crystal of infinite dimensions, (eq. [12] in Ref. 7):

$$T_m(\infty) = \Delta H^*/\Delta S^* = (68.9 \pm 0.4) \text{ deg C.}$$

The excess enthalpy of the melt ΔH^* with respect to the crystal amounts at $T_m(\infty)$, per monomer unit (eq. [10] in Ref. 7):

$$\Delta H^*[T_m(\infty)] = 2.07 \text{ Kcal/mole} \simeq 47.0 \text{ cal/g}$$

its value at the chosen reference temperature $T_o = 61.2$ °C being:

$$\begin{aligned}\Delta H^*(T_o) &= \Delta H^*[T_m(\infty)]\\ &\quad - \Delta C_p[T_m(\infty) - T_o]\\ &= 2.05 \text{ Kcal/mole}\end{aligned}$$

Surface free energies

a) Extended chain crystal ($n = 0$)

Molar excess free energy of a pair of chain ends with respect to the crystal, at T:

$$2\sigma_{e,e}(n = 0, T) = \Delta H_e - T\Delta S_e$$

ΔH_e and ΔS_e being supposed temperature independent.

$$\Delta H_e/2 = (4.18 \pm 0.22)\ \text{Kcal/mole; [10] in (7)}$$

$$\Delta S_e - R\ ln\, C = (20.3 \pm 0.3)\ \text{cal/deg. mole;}$$
$$\text{[12] in (7)}.$$

Thus at $T_m(\infty)$:

$$2\ \sigma_{e,e}[n = 0,\ T_m(\infty)] + RT_m(\infty)\ ln\ C$$
$$= 1.42\ \text{Kcal/mole;}$$
$$\text{[14] in (7)}$$

and at T_o:

$$\sum{}^{+}(0,\ T_o) = 2\ \sigma_{e,e}\,(n = 0,\ T_o)$$
$$+ RT_o\ ln\ C = 1.57\ \text{Kcal/mole;}$$
$$\text{[A 5] in Appendix 1}.$$

If $3/4 < C < 3$,

$$0.34 < \sigma_{e,e}[n = 0,\ T_m(\infty)]$$
$$< 0.81\ \text{(Kcal/mole); [16] in (7)}$$

and

$$0.42 < \sigma_{e,e}\,(n = 0,\ T_o)$$
$$< 0.88\ \text{(Kcal/mole); [14]}.$$

b) Folded chain crystals ($n \geqslant 1$)

$$2\ \sigma_{e,\,e}\,(n \geqslant 1,\ T_o) + RT_o\ ln\ C$$
$$= 2.15\ \text{Kcal/mole;} \qquad [10]$$

Molar excess free energy of one chain fold with respect to the crystal, at T_o:

$$2\ \sigma_{e,\,f}\,(T_o) = 1.38\ \text{Kcal/mole.} \qquad [11]$$

If $3/4 < C < 3$

$$0.71 < \sigma_{e,\,e}\,(n \geqslant 1,\ T_o)$$
$$< 1.17\ \text{Kcal/mole} \qquad [13]$$

thus

$$2\ \sigma_{e,\,e}\,(n \geqslant 1,\ T_o) - 2\ \sigma_{e,\,e}\,(n = 0,\ T_o)$$
$$= 0.58\ \text{Kcal/mole}. \qquad [12]$$

Conversion factor of surface free energies from molar units into erg/cm^2:

$$1\ \text{Kcal/mole} = (4.18\ 10^{10}/6.02\ 10^{23})\ N_o$$
$$\simeq 32.5\ \text{erg/cm}^2$$

N_o being the number of chains in a cross sectional area of 1 cm^2, *viz.* $10^{14}/A_o$ cm^{-2}.

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Summary

Melting temperature T_m and enthalpy of fusion have been measured, by DSC, for folded chain crystals of low molecular weight poly(ethylene-oxide) fractions ranging from 3000 to 10000. These crystals are formed by molecules folded a small integer number, *n*, of times and show unusual thermal stability on heating. The rates of chain unfolding during isothermal crystal growth and subsequent heating were measured and a reliable stability criterion could be defined for folded chain polymer crystals.

Extending the theoretical treatment of *Flory* and *Vrij* to folded chain crystals and using T_m data, a reasonable estimate was derived for the respective surface free energy contributions of chain ends and chain folds. The results suggest considerable hydrogen bonding between OH end groups, with a bonding energy of 3.1 Kcal/mole, when the crystal surface contains only chain ends. Hydrogen bonding is essentially destroyed by chain folding. Further analysis leads to an estimate of the contour length of cilia, associated with chain ends and to that of chain folds containing, on average, 2.8 and 3.5 monomer units respectively. Chain folds must thus be sharp involving adjacent re-entry. Finally, an analytical expression is derived showing the separate dependence of T_m on chain length and *n*, parameters which determine the crystal thickness *L*. Critical comparison of this relationship to that commonly used for determining surface free energies from linear T_m vs $1/L$ plots shows that the latter only applies accurately to chains of infinite length and to crystals of thickness larger than a critical value L^*.

Résumé

La température T_m et l'enthalpie de fusion ont été mesurées sur des cristaux à chaines repliées de fractions de polyoxyéthylène, de masse moléculaire variant entre 3000 et 10000. Ces cristaux sont constitués par des molécules repliées un nombre *n* entier de fois et ils ont une stabilité thermique inhabituelle. La vitesse de dépliement des chaines a été mesurée lors de la croissance isotherme des cristaux et du chauffage consécutif et l'on a pu définir un critère de stabilité pour des cristaux à chaines repliées.

En étendant la théorie de *Flory* et *Vrij* aux cristaux à chaines repliées et en utilisant les valeurs de T_m on a pu estimer les contributions respectives des bouts de chaine et des repliements à l'énergie libre superficielle. Les résultats suggèrent un couplage important, par liaison hydrogène entre les groupes terminaux OH lorsque la surface des cristaux est constituée entièrement de bouts de chaine, l'énergie de couplage étant de 3,1 Kcal/mole. Ce couplage disparait pratiquement par le repliement des chaines. L'analyse des résultats permet aussi d'estimer la longueur des bouts de chaines et celle

des repliements qui émergent du réseau cristallin: ils sont formés, respectivement de 2,8 et 3,5 unités de monomère, en moyenne. Les repliements sont serrés et relient des positions adjacentes du réseau. On déduit finalement une expression de T_m en fonction de la longueur des chaines et de n, paramètres qui déterminent l'épaisseur L du cristal. La comparaison critique de cette relation avec celle généralement utilisée pour déterminer l'énergie libre superficielle, impliquant une variation linéaire de T_m avec $1/L$, montre que cette dernière ne s'applique en toute rigueur qu'aux chaines de longueur infinie et aux cristaux d'épaisseur supérieure à une valeur critique L^*.

References

1) *Arlie, J. P., P. A. Spegt* and *A. E. Skoulios,* Makromol. Chem. **99**, 160 (1966).

2) *Arlie, J. P., P. A. Spegt* and *A. E. Skoulios,* Makromol. Chem. **104**, 212 (1967).

3) *Spegt, P.,* Makromol. Chem. **140**, 167 (1970).

4) *Spegt, P.,* Makromol. Chem. **139**, 139 (1970).

5) *Kovacs, A. J.* and *A. Gonthier,* Kolloid-Z. u. Z. Polymere **250**, 530 (1972).

6) *Wunderlich, B.,* Thermochim. Acta **4**, 175 (1972).

7) *Buckley, C. P.* and *A. J. Kovacs,* Progr. Colloid & Polymer Sci. **58**, 44 (1975).

8) *Takahashi, Y.* and *H. Tandokoro,* Macromolecules **6**, 672 (1973).

9) *Vidotto, G., D. Lévy,* and *A. J. Kovacs,* Kolloid Z. u. Z. Polymere **230**, 289 (1969).

10) *O'Neill, M. J.,* Analytical Chemistry **36**, 1238 (1964).

11) *Ginnings, D. C.* and *G. T. Furukawa,* J. Am. Chem. Soc. **75**, 522 (1953).

12) *Hellmuth, E.* and *B. Wunderlich,* J. Appl. Phys. **36**, 3039 (1965).

13) *Kovacs, A. J., A. Gonthier,* and *C. Straupé,* J. Polymer Sci. Part C, **50**, 283 (1975).

14) *Gonthier, A.,* Thèse, U. L. P. (Strasbourg, 1973).

15) *Lotz, B.* and *A. J. Kovacs,* Kolloid-Z. u. Z. Polymere **209**, 97 (1966).

16) *Beech, D. R., C. Booth, D. V. Dogdson, R. R. Sharpe,* and *J. R. S. Waring,* Polymer **13**, 73 (1972).

17) *Mandelkern, L.,* Crystallization of Polymers, p. 228 (1964).

18) *Hoffman, J. D.* and *J. J. Weeks,* J. Res. Nat. Bur. Stds. **66 A**, 13 (1962).

19) *Flory, P. J.* and *A. Vrij,* J. Am. Chem. Soc. **85**, 3548 (1963).

20) *Hoffman, J. D.,* S. P. E. Trans. **4**, 1 (1964).

21) *Hoffman, J. D.* and *J. J. Weeks,* J. Chem. Phys. **37**, 1723 (1962).

22) *Ashman, P. C.* and *C. Booth,* Polymer **13**, 459 (1972).

23) *Beech, D. R., C. Booth, C. J. Pickles, R. R. Sharpe,* and *J. R. S. Waring,* Polymer **13**, 246 (1972).

24) *Broadhurst, M. J.,* J. Res. Nat. Bur. Stds. **70 A**, 481 (1966).

25) *Beaumont, R. H., B. Clegg, G. Gee, J. B. M. Herbert, D. J. Marks, R. C. Roberts,* and *D. Sims,* Polymer **7**, 401 (1966).

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