

The investigation of solution-crystallized polyethylene by slow calorimetry

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Abstract

Single crystals of low molar mass polyethylene (PE) have been grown and dissolved in decalin. A C80 calorimeter was used to follow the heat flow during dissolution and crystallization. The aim of this study was to determine if new information on this well investigated subject could be obtained using exactly controlled conditions for the phase change. These conditions were: leaving the crystals in their mother solution for analysis, recording the dissolution traces in an unusually slow temperature ramp ($0.2\text{--}12\text{ K h}^{-1}$), following the growth of the crystals continuously during the whole crystallization process and obtaining very accurate enthalpies for the phase change. Three new results have been found: a high-temperature phase change occurs in the solution on cooling and on heating, with a corresponding change in enthalpy of $40\text{--}50\text{ J g}^{-1}$ which gives new information on the phase composition of low molar mass PE and on the interlamellar phase; the change of growth rate during crystallization is found to be linear with time; and for crystals grown at high T_c , two kinetics of dissolution/crystallization are observed. The first result is attributed to strain in chains, and the third to the dissolution/crystallization of the (100) face in larger crystals which have a truncated lozenge shape.

INTRODUCTION

Crystals of linear PE of different morphologies have been grown from the melt or from solution. The crystals grown from the melt or from solution have folded chains but those grown from the melt under high pressure have an extended chain morphology. The temperature of crystallization T_c is an important parameter in crystal growth and lamellar thickness. Growth from dilute solution gives regular crystals whose characteristics can be changed by the concentration and T_c . PE crystals have been investigated by a variety of techniques [1,2] at room temperature

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(light and electron microscopy, density, X-ray diffractometry, Raman and NMR spectroscopies) to analyze their morphology and phase content (orthorhombic crystals, amorphous and interlamellar phases). Important information on crystals can also be obtained by melting them. The parameters obtained, T_m and Δh_m , respectively the temperature and enthalpy of fusion, provide information on the phase content of the sample but are rather structure-insensitive. The dissolution temperature T_d and the enthalpy of dissolution Δh_d give the same information. The state of knowledge concerning the fusion of PE, including the concepts of equilibrium phase change, of superheating and of strained phases, as well as a review of experimental results up to 1978 can be found in Volume 3 of *Macromolecular Physics* [3]. More recent work has focussed on specific points such as the effect of crystallization conditions (solvent, solution concentration, molar mass, T_c) on crystal habits [4, 5], crystal growth [6–11], crystal melting [12–15] and on model molecules such as the long-chain alkanes [16]. The discovery that PE was highly drawable when grown in stirred or high molar mass solutions led to new avenues of research. The conditions for fiber growth, the properties of fibers, and the origin of gel formation have all been investigated [17–19]. A recent model for gel formation [20] was the outcome of a new effect found with the C80 calorimeter, a sensitive calorimeter suited for solution work which was also used in the present investigation.

Thermal analysis is almost exclusively carried out by fast DSC on dried samples, although calorimeters adapted to slow heating and to solution work have been available for some time. Fast heating leads, in general, to ambiguous baselines and uncertain enthalpies of fusion. This was illustrated recently by the results for the same sample analysed in different laboratories which revealed a wide range of enthalpies of melting. As a consequence, fast DSC is frequently used to measure accurately only T_m , rather than T_m and Δh_m . Fast heating has also the disadvantage of by-passing the slow phase changes likely to occur in long-chain molecules.

The present work illustrates the advantages of using calorimetry differently to gain new insights into the process of fusion and the solution properties. The differences reside in following phase changes in solution using a slow temperature ramp.

The fact that the crystals are seeded, grown and analyzed by way of their dissolution traces in the calorimeter, with the process being repeated on the same solution under different conditions, leads to unequalled accuracy in T_d , Δh_d and the thermal history. Perhaps the most important aspect of solution work as illustrated by the previous calorimetry of gels and confirmed with low molar mass materials, is that the accurate determination of enthalpies permits the detection of anomalies and their interpretation in terms of new effects. A connection between the heterogeneity or structure

in dilute solutions of high and low molar mass samples can be made. Slow calorimetry and solution work brings more understanding to two points of polymer physics, namely the stable association of chains in solution, which leads to gels or aggregates, and the structure of chains at the interface of crystals, which remains ambiguous despite considerable data accumulated over four decades.

EXPERIMENTAL

Materials

The linear polyethylene PE sample used was PE 1483 from NIST ($M_w = 32\,000$, $M_w/M_n = 1.11$). The solvent was decalin; the commercial mixture of cis and trans isomers from Aldrich (purity higher than 99.5%) was used without further purification.

Apparatus

The C80 calorimeter from Setaram (Lyon, France) is a sensitive DSC apparatus which combines the features of the stable, sensitive Calvet-type apparatus with those of a scanning instrument. It can accommodate large size cells (8 cm^3) and is equipped with a rotating mechanism. Due to the low noise (about $4\ \mu\text{W}$), the small heat flows evolved (less than $40\ \mu\text{W}$), for instance in a crystallization, give reliable heats even after integration over hours. An extra isolating cover was installed to minimize heat losses when working at high temperatures. In the present work, the values of the heating and cooling rates v are limited to between 0.2 and $18\ \text{K h}^{-1}$.

Medium or high molar mass solutions

The dissolution and crystallization traces of solutions of medium and high molar mass have been followed for several cycles [21]. It was found that the characteristics of the traces for the same T_c or the same T_{max} were dependent on the number of cycles. The C80 calorimeter is well suited to following the change of state of the solution during the dissolution/crystallization cycles. The succession of cycles has the effect of reducing the entanglement concentration, the important step in this being the slow crystallization in a temperature ramp [20]. The investigation of gels in the calorimeter is straightforward if the temperatures of gel formation are above room temperature. The dissolution trace was found to be an

accurate criterion of gel formation being more reliable than the flowing/non-flowing characteristics of the system.

Methods

Sample preparation

The samples (polymer or polymer + solvent) were contained in glass tubes sealed under N_2 . In order to eliminate traces of oxygen from the solution, a current of N_2 was blown through the liquid for 2 h. The absence of carbonyl groups after a long thermal history was verified by IR analysis. The polymer sample mass varied from 4 to 20 mg, and the solvent volume ranged between 2 and 4 cm^3 . The reference cell contained the same amount of solvent as the sample cell. The glass tubes were introduced in the stainless steel cells and precautions were taken to prevent their displacement when rotation of the calorimeter was applied.

Cycles of dissolution/crystallization

The calorimeter was used to prepare the first solution, to follow the thermal history required for self-seeding, to record the heat flow during crystallization (isothermal or in a temperature ramp) and to analyze the dissolution traces of the crystals formed. The advantage of using the calorimeter for all the stages in crystal formation/dissolution is that the thermal history is exact. For example, the self-seeding was performed on a solution for which both the maximum temperature reached and the rate at which the solution was raised to the maximum temperature used for self-seeding are known. Nuclei, thought to be made of the higher molar mass molecules, were found to be reinforced by slow heating. The reinforcement of nuclei has the effect of increasing the rate of crystallization. Reliability and expediency are added advantages because the same solution was used to grow crystals under different conditions (T_c , T_s). The number of dissolution/crystallization cycles pertinent to a given crystallization was recorded. For low molar mass crystals, it was found that the dissolution trace reflects the conditions of the last crystallization and, consequently, does not depend on the number of cycles for which the experiment was performed; this is not the case when the sample contains a sizable fraction of high molar mass molecules.

Stirring was always used for the first dissolution. The stirring of solutions of high or medium molar mass samples is known to favor the growth of fibrous crystals. Under the solution conditions of molar mass and concentration used here, however, stirring was found to accelerate moderately the crystallization, but to have no effect on the dissolution trace.

Self-seeding

The seeds were formed by crystallization at 81°C. The solution was left undisturbed at that temperature until the heat flow signal was constant. It was then heated with stirring to T_s and held there for 30 min before cooling to the chosen value of T_c at which the trace was recorded. The heating rates for the dissolution of seeds were 6 K h⁻¹ for $T_s = 110^\circ\text{C}$ and 0.2 K h⁻¹ for $T_s = 96$ and 93°C.

Crystallization

The response time τ of the calorimeter to a constant power P_0 can be calculated by calibration with an electric current. The value of τ (440 s) found by assuming that

$$[P(t)/(W)] = P_0[1 - \exp(t - t/\tau)]$$

implies that heat flow $P(t)$ evolved over times longer than τ , corresponds to the growth in mass of the crystals $G_m(t)$, which is related to $P(t)$ by

$$[G_m(t)/(g\ s^{-1})] = [P(t)/(J\ s^{-1})]/[\Delta h_0/(J\ g^{-1})] \quad (1)$$

where Δh_0 is 293 J g⁻¹, the enthalpy of fusion of perfect crystals. The growth in mass of crystals $G_m(t)$ depends on the product of the number of nuclei N_s , and the growth factor of an individual crystal, dm/dt . N_s depends on the seeding temperature and dm/dt on its diameter r , thickness l , density d and a geometrical factor k

$$G_m(t) = N_s\ dm/dt = kN_s\ r\ dr/dt\ l\ d \quad (2)$$

A simple expression for $r(t)$ will be presented below.

In order to determine accurately the enthalpy of crystallization, the crystal growth must be neither too rapid nor too slow. The complete crystallization has been analyzed for a range of times between 3 and 20 h. By changing T_s , the growth in mass can be modified. For a 0.1% solution, for instance, the growth can be followed up to $T_c = 88^\circ\text{C}$ for $T_s = 93^\circ\text{C}$, but only to $T_c = 83^\circ\text{C}$ if the nuclei have been reduced by raising T_s to 110°C.

Enthalpy of dissolution and enthalpy of fusion

When a semi-crystalline polymer with a enthalpy of fusion Δh_m is dissolved in a solvent, the heat evolved Δh_d is

$$\Delta h_d = \Delta h_m + \Delta h_{\text{mixing}}$$

The Δh_{mixing} value of PE in decalin can be estimated from the enthalpy

of mixing of decalin in linear alkanes. It is found to be positive and equals 2 J g^{-1} . Consequently, Δh_d can be equated with Δh_m , Δh_{mixing} being neglected in view of the large value of Δh_m (about 250 J g^{-1}).

RESULTS AND DISCUSSION

Four aspects of our research are reported here

(i) The conditions for recrystallization in solution will be illustrated in Figs. 1–3, and the well-known relationships between T_d and T_c and between Δh_d and T_c are given in Fig. 4 and Table 1, with the results of the extrapolated values of $T_{d,0}$ and $\Delta h_{d,0}$.

(ii) A new feature of slow melting/crystallization, which reveals the presence of a high-temperature endotherm (called Fraction III) above $T_{d,0}$, can be seen in Figs. 5 and 6.

(iii) The special characteristics of the dissolution trace of crystals grown at high T_c are displayed in Fig. 7.

(iv) The analysis of a crystallization curve leading to the calculation of the growth rate of the crystals during the crystallization time is given in Fig. 8.

The traces in Fig. 2 illustrate the limit to the attribution of the shape of a trace to a physical phenomena when these traces are obtained in a different temperature ramp. From our knowledge of the slow kinetics of recrystallization in dilute solution near T_d , the trace in Fig. 2(a) was interpreted as showing the dissolution of crystals without recrystallization. However, the trace can also be interpreted as the overlapping of the two curves seen at lower ν in Fig. 2(b) and (c).

Recrystallization, T_d – T_c relationship and enthalpies of fusion

Recrystallization

An illustration of the effect of T_c on recrystallization is given in Fig. 1 using $\nu = 6 \text{ K/h}^{-1}$. The thinner and less stable crystals formed at $T_c = 80^\circ\text{C}$ partially dissolve at $T_d = 90^\circ\text{C}$, recrystallize, and dissolve as thicker crystals at $T_d = 93^\circ\text{C}$, as seen in Fig. 1(a) ($c = 1.2\%$). The crystals grown from the same solution at 84°C dissolve at an intermediate temperature without recrystallization (Fig. 1(b)). The solution concentration, ν and T_c are the parameters which govern recrystallization. Figure 2, (a), (b), (c), shows the dissolution traces for crystals grown at $T_c = 80^\circ\text{C}$ from a 0.1% solution, dissolved at $18, 6$ and 1 K h^{-1} , respectively. It can be seen that recrystallization does not occur at 18 K h^{-1} , but then increases for $\nu = 6$ and 1 K h^{-1} .

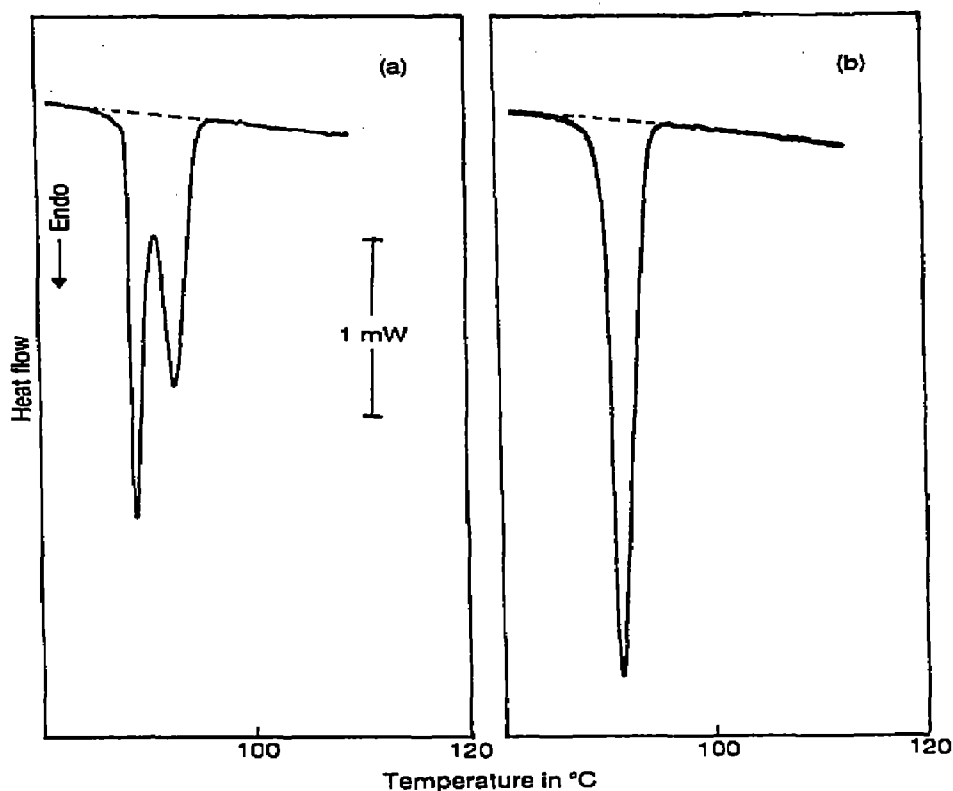


Fig. 1. Dissolution traces of PE crystals grown in decalin at $T_c = 80^\circ\text{C}$ (a) and 84°C (b); $\nu = 6 \text{ K h}^{-1}$, $c = 1.2\%$. Reorganization occurs only at the lower T_c .

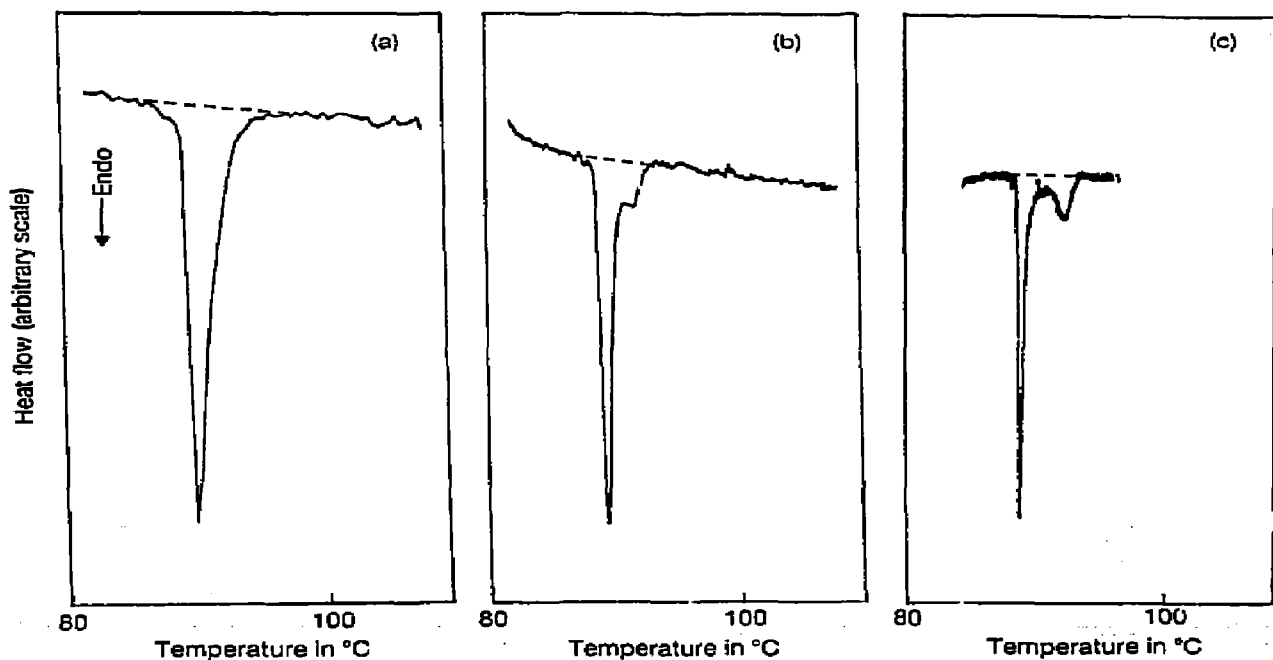


Fig. 2. Dissolution traces of PE crystals grown in decalin at $T_c = 80^\circ\text{C}$ and $c = 0.1\%$ at three values of ν : (a) 18; (b) 6; and (c) 1 K h^{-1} . Reorganization is observed when ν diminishes.

The crystals formed in the more dilute solution are more stable, because at 6 K h^{-1} recrystallization is more important for the 1.2% solution (Fig. 1(a)) than for the 0.1% solution (Fig. 2(b)). By reducing the temperature ramp even more, a separation of the steps distinguished in Figs. 1 and 2 can be achieved. This is shown in Fig. 3 where crystals grown at 80°C (a) and 81°C (b) were dissolved at $\nu = 0.2 \text{ K h}^{-1}$. Under the present conditions of concentration and rate of heating, the thickening of the lamellae cannot exceed a certain value, estimated at $l = 190 \text{ \AA}$ from the end of the second endotherm of dissolution (93.5°C). This value is lower than the value extrapolated for infinitely thick lamellae which is found at 96.6°C as discussed below (Fig. 4). The end of the dissolution occurs at the same temperature for the crystals grown at 80 and 81°C , but the size of the dissolution endotherm of the recrystallized crystals is larger for the crystals grown at 80°C (Fig. 3(a)). The exotherm of recrystallization seen between the endotherms of dissolution seems to be more important for the crystals formed at 80°C . Because the traces correspond to the same sample tube dissolved under the same conditions, the baseline has been drawn in the same manner for both. The ambiguity in the baseline of Fig. 3(a) must arise from the overlapping of the endotherms and exotherms which occur over a range of temperatures during the dissolution/thickening of the less stable crystals grown at 80°C .

T_d – T_c relationship and enthalpies of dissolution Δh_d

Because the dissolution traces show two peaks, either for low T_c or high T_c , and one peak at intermediate T_c , some explanation must be given on the choice of T_d used for the T_d – T_c relationship in the case of complex dissolution traces. At low T_c , i.e. at $T_c = 80$ and 81°C , the T_d of the largest peak at low T is taken as representing the dissolution temperature of the thin crystals (Fig. 1(a) and Fig. 2(b) and (c)). At intermediate T_c , i.e. at $T_c = 82, 83, 84^\circ\text{C}$, there is no ambiguity in the trace. At high T_c , i.e. at $T_c = 85, 86, 87$ and 88°C , the T_d of the highest peak is chosen because at these temperatures and concentrations thickening is known not to take place. An explanation is given below for the presence of the shoulder at low T . Table 1 lists the T_d and Δh_d values at 6 K h^{-1} for crystals grown at two concentrations versus T_c . The last column gives the lamellar thickness, estimated from the literature [5] to vary between 135 and 182 \AA . The T_d values are plotted against T_c in Fig. 4(a) for the 0.1% (●) and 1.2% (Δ) solutions. A standard procedure to obtain $T_{d,0}$ is to extrapolate T_d to its intersection with the line $T_d = T_c$. Using the data for $c = 0.1\%$, $T_{d,0}$ is found to be 96.6°C , in agreement with previous work on the dissolution of extended-chain crystals [3]. In Fig. 4(a), the T_d values for $c = 1.2\%$ are higher than those for $c = 0.1\%$. The difference persists, even for lower values of ν ; hence it is not due to the rate of dissolution. An effect of c on T_c is to be expected from a eutectoid crystallization of PE. The fact that Δh_d is

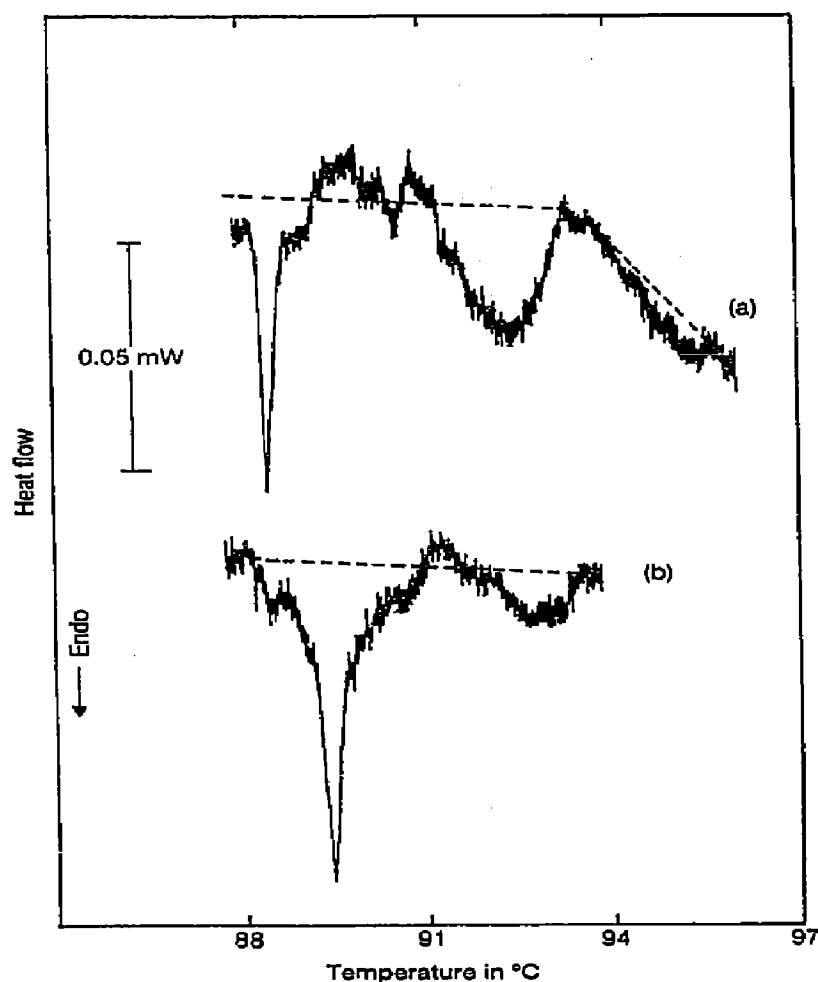


Fig. 3. Dissolution traces of PE crystals grown in decalin at $T_c = 80^\circ\text{C}$ (a) and 81°C (b) at a very low value of v (0.2 K h^{-1}). The exotherm of recrystallization to thicker lamellae is seen between the two melting endotherms.

also affected by the concentration may be an indication that entanglements in the more concentrated solution have an effect in raising T_d . The variation of lamellar thickness versus T_c can be calculated from the $T_d(T_c)$ curve by fitting one point to a given lamellar thickness.

Figure 4(b) shows the Δh_d values plotted against T_c for two concentrations, $c = 0.1\%$ (\bullet) and $c = 1.2\%$ (Δ). Over a 10 K range of T_c ($80\text{--}90^\circ\text{C}$), the enthalpy of fusion of the orthorhombic crystals increases by about 8% when the lamellar thickness increases by about 60 \AA . The difference of Δh_d in Fig. 4(b) shows that the effect of concentration is as important as the effect of T_c on the enthalpy of dissolution of the crystals. The diminution of the enthalpy of dissolution when c increases is associated with stable links between crystals. These links persist in solution and have an enthalpic content corresponding to the so-called, Fraction III, as explained below.

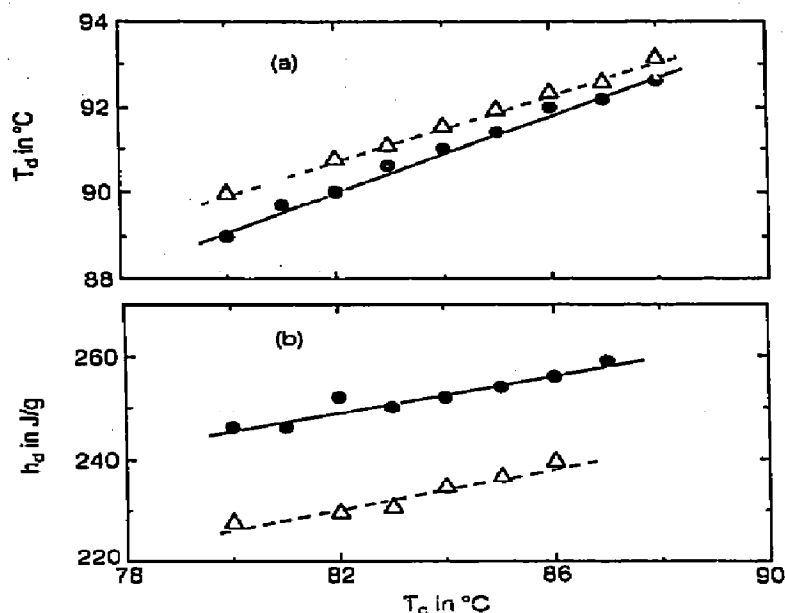


Fig. 4. Correlation between T_d and T_c (a) and between Δh_d and T_c (b) for PE crystals grown in decalin, $\nu = 6 \text{ K h}^{-1}$; \bullet , $c = 0.1\%$; Δ , $c = 1.2\%$.

The variation with T_c of Δh_m for crystals of similar molar mass (molar mass = 11,600) [14] also grown in dilute solution, is similar to that of Δh_d . The fact that the crystals were dried before the measurement of Δh in ref. 14 apparently did not damage the surface of the crystals, as has been sometimes suggested.

TABLE I

Characteristics of dissolution of PE crystals (NIST, 1483) grown in 0.1% and 1.2% Decalin solutions, heating rate 6 K h^{-1}

$T_c/^\circ\text{C}$	0.1% Solution		1.2% Solution		$l/\text{\AA}$ ^a
	$T_d/^\circ\text{C}$	$\Delta h_d/(\text{J g}^{-1})$	$T_d/^\circ\text{C}$	$\Delta h_d/(\text{J g}^{-1})$	
80	89.0	245	90.0	228	135
81	89.7	246			139
82	90.0	252	90.8	230	144
83	90.6	250	91.1	231	150
84	91.0	252	91.6	235	156
85	91.4	254	92.0	227	163
86	92.0	256	92.4	240	169
87	92.2	259	92.6	—	176
88	92.6	—	93.2	—	182

^a Estimated from ref. 5 using $l(T_c)_{\text{decalin}} = l(T_c - 5)_{\text{styrene}}$.

The high-temperature endotherm revealed by a slow temperature ramp

The existence of a high-temperature endotherm was first discovered [20] during the dissolution of UHMWPE in decalin. On cooling, a high-temperature exotherm was found, from the clear solution, with about the same change in enthalpy as the dissolution endotherm ($50\text{--}80\text{ J g}^{-1}$). This exotherm, which indicates that some organization takes place in solution, is believed to be the origin of thermoreversible gels. It has been called Fraction III. Fraction III has also been found on melting either nascent or recrystallized PE samples. An essential condition under which to find Fraction III is the very slow increase or decrease of temperature. Otherwise, the phase-change does not occur or is incomplete. For instance, Fraction III cannot be seen on melting UHMWPE if ν is higher than 12 K h^{-1} [22].

Figure 5(a) and (b) shows the melting and crystallization traces of

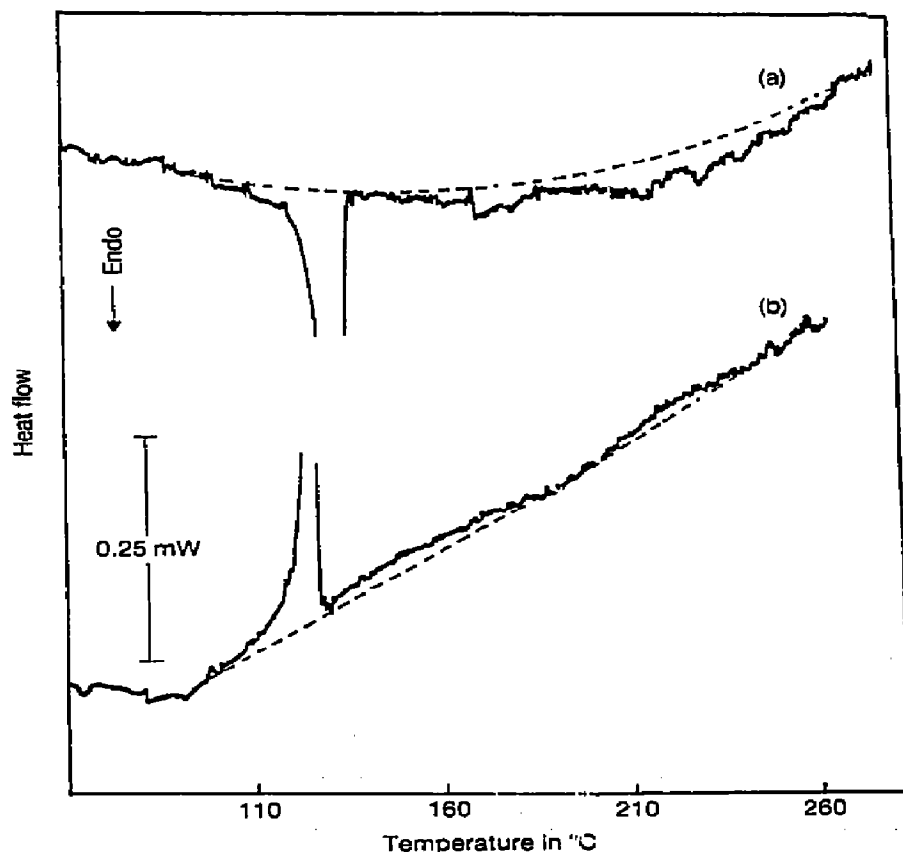


Fig. 5. Melting (a) followed by crystallization (b) of PE showing the new high- T phase change (Fraction III) revealed by slow scanning (6 K h^{-1}): $\Delta h_{\text{fusion}} = 45\text{ J g}^{-1}$; and $\Delta h_{\text{cryst}} = 45\text{ J g}^{-1}$.

TABLE 2

Characteristics of melting and crystallization of PE 1483 at 6 K h⁻¹

	$T_m/^\circ\text{C}$	$\Delta h_m/(\text{J g}^{-1})$	$\Delta h_m/(\text{J g}^{-1})^a$	$\Delta h_{\text{tot}}/(\text{J g}^{-1})$
Dry polymer				
Melting	131.7	245 (95-142)	45 (142-266)	290
Crystallization	125.7	240 (96-129)	45 (129-240)	285
In decalin ($c = 0.1\%$) ^b				
Dissolution	89.0	245 (86-94)	55 (100-161)	300
Crystallization	75.4	240 (69-78)	60 (95-140)	300

^a Δh_m of high- T fraction. ^b PE crystals grown at $T_c = 80^\circ\text{C}$.

sample PE 1483 at 6 K h⁻¹. In addition to the main peaks, one can distinguish two changes in the heat flows corresponding to a slow kinetics of phase change situated between 142 and 266°C for the fusion, and between 240 and 129°C for the crystallization. The values of the changes in enthalpy are given in Table 2. The name, Fraction III, for high- T fraction is derived from the presence of three successive endotherms, observed in nascent UHMWPE melted at 1 K h⁻¹, the first two being Fraction I, the low- T endotherm, and Fraction II, the phase change of the orthorhombic crystals. The low- T endotherm evolved at temperatures lower than the main peak has a slow kinetics. In ref. 22, this has been associated with the low molar mass fraction of the sample. Recent work on films [23] suggests that it pertains to that part of the network which undergoes a phase change at low temperature. This result indicates that high molar mass and polydispersity are not prerequisites for finding a high-temperature phase change in linear PE. In Fig. 5(a) and (b), due to the relatively high ν and the narrowness of the molar mass distribution of the sample, Fraction I is not seen clearly.

Figure 6 shows the dissolution trace at 6 K h⁻¹ of crystals grown at $T_c = 80^\circ\text{C}$; it is comparable to the melting trace of Fig. 5(a), with the slow dissolution endotherms at high T separated by an arrested dissolution. The corresponding changes in enthalpy and the intervals of integration used are given in Table 2. The kinetics of the phase change of Fraction III is solvent-dependent. In decalin, the endotherm spread over a larger temperature interval than in cyclohexane [21]. Note that the high- T endotherm can also be seen in the very slow dissolution presented in Fig. 3, but due to the slow temperature ramp, the phase change here occurs between 94.0 and 95.5°C. The change in enthalpy of Fraction III is about 50 J g⁻¹ in both cases. The high- T endotherms of Figs. 6 and 3 illustrate the

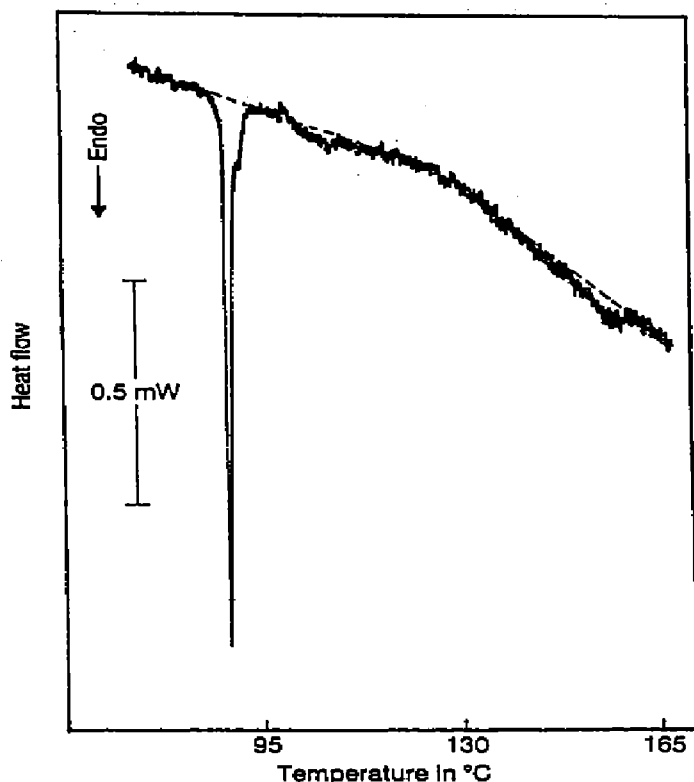


Fig. 6. Dissolution trace of PE sample ($T_c = 80^\circ\text{C}$) in decalin at $v = 6 \text{ K h}^{-1}$ showing the high- T dissolution endotherm, $c = 0.1\%$.

effect of thermal history on the time/temperature of the phase change. By raising the temperature very slowly, the time elapsed between the maximum of the main peak and the end of Fraction III is reduced from 11 h ($v = 6 \text{ K h}^{-1}$) to 8 h ($v = 0.2 \text{ K h}^{-1}$). It has been found repeatedly that changing the thermal history of the solution or of the melt has a great influence on the temperature of the phase change; these results will not be given in detail in this paper.

Much thought and experimental verification have been directed to ascertaining that the high- T effects are not related to some chemical reaction or artifacts in the technique. The following points give confidence on the interpretation of the high- T endotherms.

- (i) The effect is reversible, an exotherm being observed on cooling.
- (ii) The kinetics and temperature of the phase change can be displaced depending on the conditions. In low boiling point solvents, such as 2-methylbutane for instance, the temperature of the phase change of Fraction III starts at low temperature and overlaps with that of the fusion of the orthorhombic crystals. The overall enthalpy of dissolution is entirely evolved below $T_d = 110^\circ\text{C}$, a temperature too low to lead to degradation.

The use of a finitely divided substrate, such as Cu, has the same effect as a volatile solvent in displacing the T_u or T_m of Fraction III towards a low T .

(iii) Samples of crosslinked PE give high- T endotherms in the melt or in solution, suggesting that physical and chemical networks behave similarly.

The reason for applying a slow temperature ramp was the discovery of inconsistent results with regard to the changes in the enthalpy of the UHMWPE sample in different solvents. This led us to believe that there was a hidden endotherm in one solvent and not the other which would reestablish an equal value for the enthalpy of dissolution of the sample in the two solvents. In these solutions, the enthalpy of dissolution was too different to be explained by a solvent effect on Δh_{mixing} .

The occurrence of Fraction III provides an explanation for several ambiguous points found in the literature, one being the low value of the enthalpy of fusion of the equilibrium crystals. As reported in ref. 3, 15–20 J g⁻¹ were unaccounted for in the extrapolated values of the enthalpies obtained from very accurate melting experiments of solution-grown crystals. The present analysis confirms that indeed a small part of the chains dissolved in solution cannot crystallize as orthorhombic crystals but it reveals that they can nevertheless be analyzed through a high- T phase change.

The melting trace of Fig. 5 reveals important information on the phases of PE. It can no longer be considered as a two-phase system made of orthorhombic crystals and of disordered chains. A three-phase system describes better the polymer, as has been indicated by ¹³C analysis [24]. The analysis was made in terms of a crystalline phase, a semi-mobile interlamellar phase, and a mobile amorphous phase. The identification of Fraction III with the interlamellar phase has been proposed and quantitative evaluation of the phase content can be obtained from the melting or crystallization trace of Fig. 5 [23]. The origin of Fraction III is now thought to be an order–disorder transition in the chains of a network present in the solid [25].

The origin of Fraction III has been discussed elsewhere and it is still a subject of investigation. It has been associated with strain in semi-ordered chains where entanglements and small crystallites have an essential role to play. Current investigations [21] by ¹³C NMR and IR which give important information on the movement of chains during melting, should bring more understanding to the origin of Fraction III.

Crystals grown at high temperature

Isothermal crystallization was performed on a 0.1% solution after $T_c = 93^\circ\text{C}$. The time for complete crystallization was, respectively, 2, 4 and 8 h for $T_c = 82, 85$ and 86°C . The dissolution traces at 6 K h^{-1} are shown in

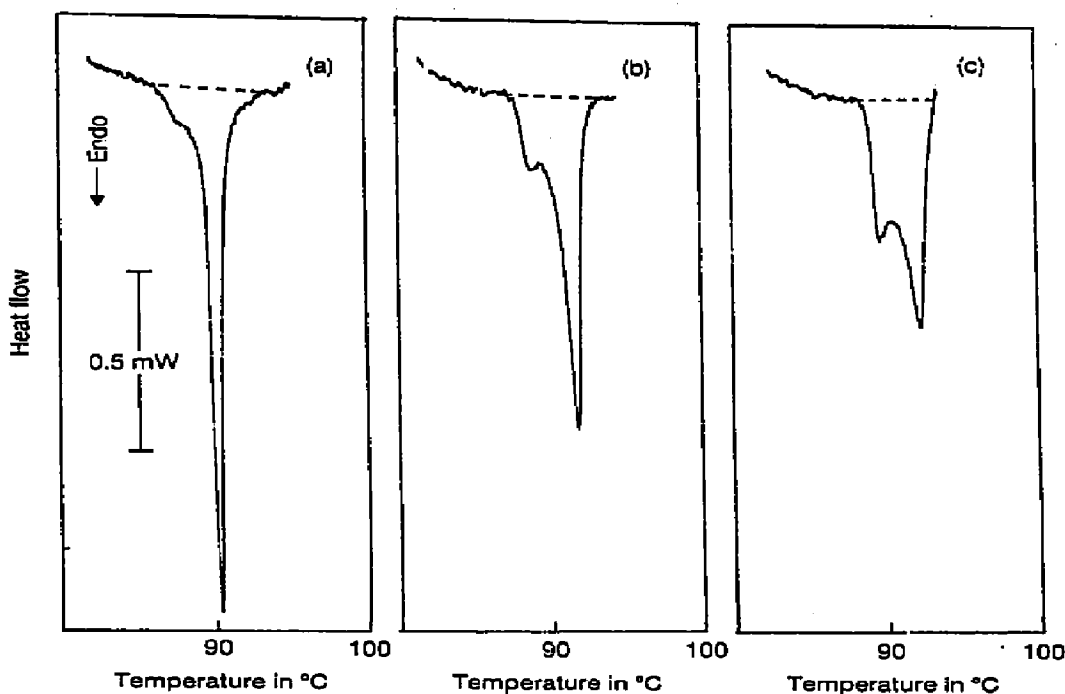


Fig. 7. Dissolution traces at 6 K h^{-1} of PE grown at high T in decalin with $T_c = 93^\circ\text{C}$, showing an endotherm at low T : (a) $T_c = 82^\circ\text{C}$; (b) $T_c = 85^\circ\text{C}$; and (c) $T_c = 86^\circ\text{C}$ ($c = 0.1\%$).

Figs. 7(a)–(c). As mentioned above, the trace for $T_c = 82^\circ\text{C}$ has a single peak while a shoulder appears at low T for $T_c = 85^\circ\text{C}$. The shoulder increases for the crystals grown at $T_c = 86^\circ\text{C}$ (Fig. 7c) and above (not shown). The main peak must represent the original lamellar thickness of the crystals because recrystallization does not occur at these high values of T_c . Consequently, the temperature of the main peak is that which has been plotted in Fig. 4(a) to establish the T_c – T_0 relationship. The peak at low T must be explained. The fact that the endotherm at low T increases with T_c suggests an interpretation which is drawn from literature results. A comparison with melting traces is necessary because dissolution traces have rarely been reported. A double peak has been found in an investigation of crystal growth at different temperatures [13]. In order to cover the gap in lamellar thickness between the values for solution-crystallized and melt-crystallized PE samples, Organ and Keller used a series of solvents different in size and solvent quality to cover a T_c range of 18 K. The crystals undergoing melting were analyzed by microscopy and DSC. The electron micrographs revealed that as T_c increases the shape of the crystals changes from a lozenge via a truncated lozenge to an oval-like shape whose ratio of the long axis over the small axis varies between 1 and 3. The crystals have three-dimensional features and their thermal stability is related to sectorization. In octane ($T_c = 95^\circ\text{C}$) for instance, the melting trace has two

peaks. With a heating rate of 300 K h^{-1} , the difference between the melting peaks is 0.9 K. The two endotherms have been associated with the different kinetics of melting of the different faces of the truncated lozenge. Microscopic observation of melting has revealed that the truncated (100) surfaces, which are only present in large crystals grown at high T , melt before the (110) faces. The two dissolution peaks observed for crystals grown in decalin may well have the same origin as those that occur in different solvents. Electron micrographs could provide a definite answer. If this is indeed the case, important information related to crystal morphology can be obtained from the dissolution traces. Firstly, the presence of the solvent and the slow heating rate can reveal double peaks that are not apparent in the melting trace. The large difference found in T_d for the different faces (about 2.5 K) could be evidence for the sensitivity of the technique to the crystal morphology. Furthermore, the relative areas of the endotherms at low and high T should then be an indication of the amount of (100) faces and, indirectly, of the crystal size because the (100) face dissolves at low T . The endotherm at low T increases from 10% to 35% when T_c increases from 82 to 86°C. Crystallization traces give similar information which will be detailed elsewhere [21]. It is worth noting that this change of shape can be obtained in a single solvent by changing T_c by 4 K only.

Crystal growth in solution

The morphology of solution-grown crystals is usually investigated on crystals left to grow slowly at the chosen T_c . Crystal growth data are obtained on unfinished crystals grown for a short time at the chosen T_c and left to grow rapidly in a second phase. Electron micrographs of crystals that were grown slowly provide a measurement of the linear growth rate $G(T_c)$ used to test crystallization theories. Self-seeding is used to regulate the number of nuclei N_s and, consequently, the size of the crystals. However, a fraction of the crystals cannot be analyzed due to overgrowth or to an effect of impurity. Information on crystal growth which would complement the electron microscopy analysis would be very valuable. In particular, it will fill a gap concerning the reorganization, the increase in perfection, and the change in shape of the crystals in the active period separating the beginning and the end of crystallization. Due to its sensitivity and its stability, the C80 calorimeter can follow the thermal effects associated with crystal growth in solution when it occurs over an adequate temperature interval (about 3–40 h). Crystallization traces have been obtained for the present system at different values of T_c . The trend of the crystallization traces is similar to that of the dissolution traces. When crystallization occurs at low T_c with a small value of N_s , the traces have only one peak. However, the traces have two peaks for slow crystallization at high T_c ($T_c > 85^\circ\text{C}$). The growth or

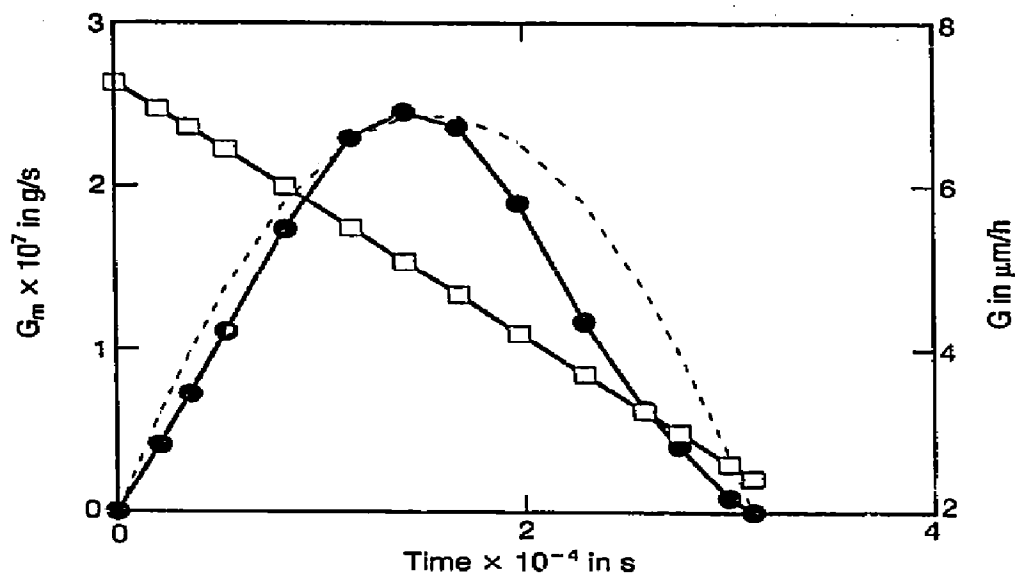


Fig. 8. Crystallization of PE in decalin at $T_c = 82^\circ\text{C}$, $T_s = 110^\circ\text{C}$ and $c = 0.1\%$; $\Delta h_c = 252 \text{ J g}^{-1}$. The two curves (●) and (---) correspond to the experimental and calculated growth in mass G_m using eqn. (6). The curve (□) shows the variation of the linear growth rate G over the time of crystallization (8h).

reorganization of the truncated (100) faces (see above) in the final stages of the isothermal crystallization could well be associated with the second peak with the slowest kinetics. The complex crystallizations will be reported elsewhere [21]; an analysis of the simple trace will be given below.

In Fig. 8, the growth in mass $G_m(t)$ in g s^{-1} is plotted against time for $T_s = 110^\circ\text{C}$ and $T_c = 82^\circ\text{C}$. The remarkable symmetry of the heat flow around the maximum suggests a simple analytical form for the linear growth rate of the crystal dr/dt

$$r = mt(1 - pt) \quad (3)$$

$$dr/dt = G(t) = m(1 - 2pt) \quad (4)$$

$$r \, dr/dt = m^2 t(1 - pt)(1 - 2pt) \quad (5)$$

Putting eqn. (5) in eqn. (2), one finds

$$G_m(t) = A_s m^2 t(1 - pt)(1 - 2pt) \quad (6)$$

where m , p and A_s are constants. A_s contains N_s , l , d and the geometric constant. The second term of eqn. 3 takes into account the decrease in linear growth rate when the crystal size increases, because of depletion of the molecules in the solution. The equations are not valid for $t > 1/2p$ because dr/dt would be negative. The value of p can be found either by the time at which $G_m = 0$ or at which G_m is maximum. By derivation of eqn. (6) and neglecting the higher order term of t , one finds that G_m is maximum for

$t = 1/6p$ and 0 for $t = 1/3p$. The comparison with the experimental curve $G_m(t)$ gives p . The value of G_m at the maximum ($=A_s m^2/12p$) permits one to obtain the parameter m and $G(t)$ when N_s and l are known. The values of N_s and l for decalin have been estimated from literature values in xylene. A shift of 5 K is required because decalin is a better solvent than xylene. The broken curve of Fig. 8 calculated from eqn. (6) shows that it is a good fit for $G_m(t)$. The linear growth rate $G(t)$ given by eqn. (4) is also plotted on Fig. 8. The dependence of $G(t)$ on solution concentration can also be calculated because the amount of polymer already crystallized is known at each time from the crystallization trace. More details on $G(t)$ and the effect of T_s , T_c and N_s on the parameters characterizing the growth will be given elsewhere [21]. The complex crystallization curves which match the dissolution curves of Fig. 7 will also be presented.

CONCLUSION

The present investigation reports the use of calorimetry in solution, using a slow temperature-ramp to analyze the growth of crystals and their dissolution. New information has resulted from this study.

- (i) The conditions of recrystallization in solution.
- (ii) The existence of a high- T endotherm which explains some previous inconsistencies in the enthalpies of fusion and other phenomena.
- (iii) The presence of an endotherm at low temperature in crystals grown at high temperature probably corresponds to the melting of the (100) face of truncated crystals.
- (iv) The determination of the variation in the linear growth of crystals during the duration of crystallization.

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