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On the morphology and crystallization kinetics of monodisperse polyethylene oligomers crystallized from the melt

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The melt crystallization of three monodisperse paraffins, $C_{294}H_{590}$, $C_{246}H_{494}$ and $C_{198}H_{398}$, has been studied optically as a function of temperature. In both $C_{294}H_{590}$ and $C_{246}H_{494}$, a distinct minimum in the rate of crystal growth has been observed, corresponding to a transition from predominantly chain-extended crystallization at high temperatures to the growth of crystals in which the molecules adopt a once-folded conformation. This change in molecular conformation is accompanied by a change in optical texture. Well below the minimum, morphologies, are spherulitic and closely resemble polyethylene. When crystals contain chain-extended molecules, highly birefringent, coarse lamellar textures develop. In $C_{198}H_{398}$, no minimum in the crystal growth rate has been observed; this system does, however, exhibit similar morphological trends to those seen in $C_{294}H_{590}$ and $C_{246}H_{494}$. Copyright © 1996 Elsevier Science Ltd.

(Keywords: monodisperse paraffins; crystallization kinetics; melt crystallized morphologies)

Introduction

The synthesis of monodisperse long-chain paraffins was pioneered by Whiting and co-workers[1,2], specifically to provide model systems on which definitive studies pertinent to problems of polymeric crystallization could be performed. Initial investigations of the crystallization behaviour of these polyethylene oligomers demonstrated the formation of lamellae, in which the molecules tend to adopt an integrally folded conformation[3,4]. In addition, a local minimum in the overall rate of crystallization was observed (at T_{min}), and associated with the onset of chain folding[5,6], which first occurs at the temperature T^*. T^* is a theoretical parameter, corresponding to the highest temperature at which once-folded molecular conformations are thermodynamically stable. As such, its precise value will depend both upon the model being used and the values chosen for included experimental parameters. T_{min} corresponds to the temperature of the minimum in the observed crystallization or crystal growth rate and is determined experimentally.

In this paper, the crystallization behaviour of three polyethylene oligomers is described as functions of crystallization temperature and molecular length. Morphological variations are reported together with crystal growth rates, obtained by direct optical measurement. Unlike published data concerning the overall rate of crystallization, these results are not influenced by nucleation processes and, therefore, constitute a more stringent test of proposed crystal growth theories[7-9].

Experimental

Three monodisperse paraffins $C_{294}H_{590}$, $C_{246}H_{494}$ and $C_{198}H_{398}$ were examined (to be referred to subsequently as C294, C246 and C198); these were prepared in a recent synthesis at the University of Durham, under the auspices of the Engineering and Physical Sciences Research Council (EPSRC) of the UK. To prepare specimens, small amounts of virgin powder were melted on a Koffler hot-bench, then transferred to a Mettler FP5 hot-stage (nitrogen atmosphere), where they were briefly melted at 145°C before being crystallized isothermally. Crystallization was monitored either by periodic photography or by recording the complete process on video tape. Growth rates at each temperature were evaluated from plots of maximum dimension against time and the quoted values were obtained by averaging data obtained, typically, from five distinct crystalline aggregates. After quenching in ice/water, appropriate samples were examined optically in transmission.

Attempts were also made to estimate the equilibrium melting temperature of each material. Self-seeding techniques were employed to produce a small number of chain-extended, high temperature crystals, which were subsequently heated at $0.2\,K\,min^{-1}$; the disappearance of birefringence was taken as an indication of the melting temperature. Similar experiments were also performed using high purity, melting point calibration standards.

Results and discussion

Figure 1 shows the crystal growth rate as a function of temperature (T_c) for C294. As T_c is reduced, the growth rate first rises, then passes through a minimum at $T_{min} = 124.5 \pm 0.5°C$, before finally increasing rapidly. The general form of this plot agrees well with complementary published results obtained by d.s.c. on specimens of C246 prepared in an earlier synthesis[5,6]. The minimum corresponds to the transition from a temperature range ($T_c > T_{min}$) where growth of chain-extended lamellae is the preferred mode of crystallization, to a condition where once-folded conformations predominate. The presence of a distinct minimum, in contrast to a local depression, is in marked contrast both to data reported by Stack *et al.*[10] and Alamo[11] and results obtained on narrow fractions of different systems[12-14].

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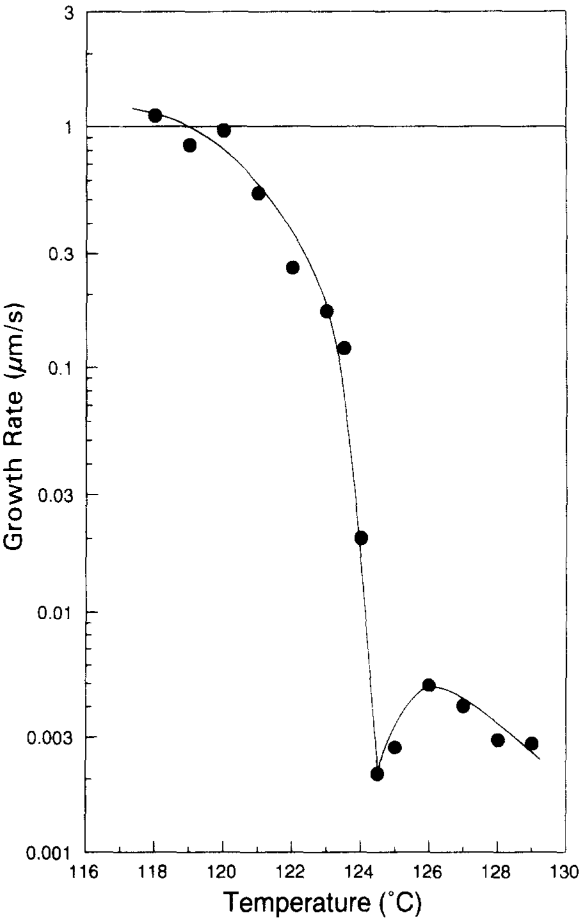

Figure 1 Variation in the average crystal growth rate as a function of crystallization temperature for C294

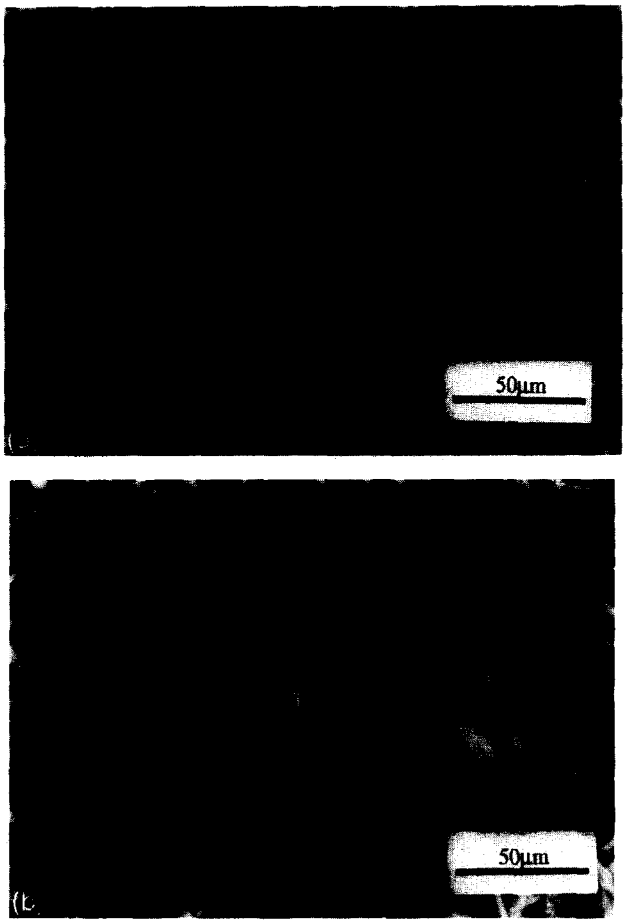

Figure 2 Transmission optical micrographs (crossed polars) showing the range of textures seen in C294: (a) a coarse polycrystalline aggregate grown at 129°C; (b) spherulites grown at 118°C

The transition from chain-extended to chain-folded crystallization [as determined by transmission electron microscopy (TEM)[15]] not only affects the rate of crystal growth, but also results in a dramatic change in the overall morphology. Extended chain crystallization of C294 at high temperatures results in coarse, highly birefringent aggregates of elliptic lamellae (*Figure 2a*). Rotation of such objects between crossed polars demonstrates that they consist of a number of distinct regions, within which the lamellae share a common orientation; the radial symmetry characteristic of spherulites is absent. A more detailed morphological study of such structures by TEM[15] has shown that these optical characteristics are a direct consequence of the absence of lamellar splay. The high macroscopic birefringence results from correlated domains in which lamellae grow parallel and adjacent. Although some lamellar branching does occur, apparently via crystallographic processes, the progressive divergence of neighbouring lamellae in response to a localized force-field in the region of a branch point, a characteristic of polymeric crystallization[16], is largely absent. At much lower crystallization temperatures, the morphologies are polymeric in their appearance; the spherulites shown in *Figure 2b* developed at 118°C.

At intermediate temperatures, there is a progressive change in morphology and crystal habit (*Figure 3*). As T_c is reduced, more complex lamellar aggregates develop, which can appear spherulitic when profuse primary nucleation has occurred (*Figure 3a*). However, comparison with *Figure 2* demonstrates that, despite its overall shape, the internal structure of the object that is arrowed more closely resembles the coarse morphologies of chain-extended growth, rather than the radically symmetric textures that occur when lamellae contain molecules that are once-folded. These structures are also composed of elliptic crystals, which become more elongated as T_c *decreases* towards T_{min}. Conversely, in polyethylene, the aspect ratio increases as the T_c *increases* towards T_m^0[17]. It has been proposed that this is a consequence of growth surfaces becoming increasingly rough as T_m^0 is approached[18]. The observation of similar behaviour in chain-extended lamellae of C294 (and the other systems considered here), in the vicinity of T_{min}, strongly suggests that a similar mechanism is operative. This is consistent with ideas of self-poisoning[18].

Although the previous discussion of morphology referred exclusively to C294, both C246 and C198 behave in a similar manner. In both, the morphological spectrum is, however, displaced to lower temperatures, due to their reduced chain lengths and T_m^0 values. Also, particularly in C246, the optical textures observed close to T_{min} imply that extended and once-folded conformations co-exist, as required for self-poisoning. *Figure 3b* shows spherulites grown at 123°C, which incorporate highly birefringent regions (arrowed). We interpret these features, which occur commonly in specimens crystallized near T_{min}, as inclusions of chain-extended lamellae within chain-folded spherulites. The occurrence of such features decreases as the crystallization temperature is reduced.

Figure 4 shows growth-rate data obtained for C246 and C198. C246 behaves like C294, but with T_{min} = 121.8 ± 0.5°C, consistent with published results[5]. Assuming that this value corresponds to T^*, the variation in this quantity as a function of molecular length can be estimated from simple secondary nucleation theory[19]. Taking into account variations in T_m^0 (see *Table 1*), but assuming that all other quantities remain constant, chain-folded lamellae should just be stable in C294 at ~125°C. This result, which is not sensitive to the precise values chosen for T_m^0 in each system[8,10], is consistent with those of *Figure 1*. Clearly, in neither system will T_{min} correspond *exactly* to T^*, but the calculations nevertheless provide a valid means of comparison (see *Table 2*).

The behaviour of C198 is markedly different. The crystal growth rate of both C294 and C246 increases by more than two orders of magnitude over the temperature interval 128–118°C whereas in C198 it is only weakly dependent on crystallization temperature. In polyethylene, the dependence can be considerably stronger[19]. Also, although a minimum in the crystallization rate of C198 was observed when this material was crystallized

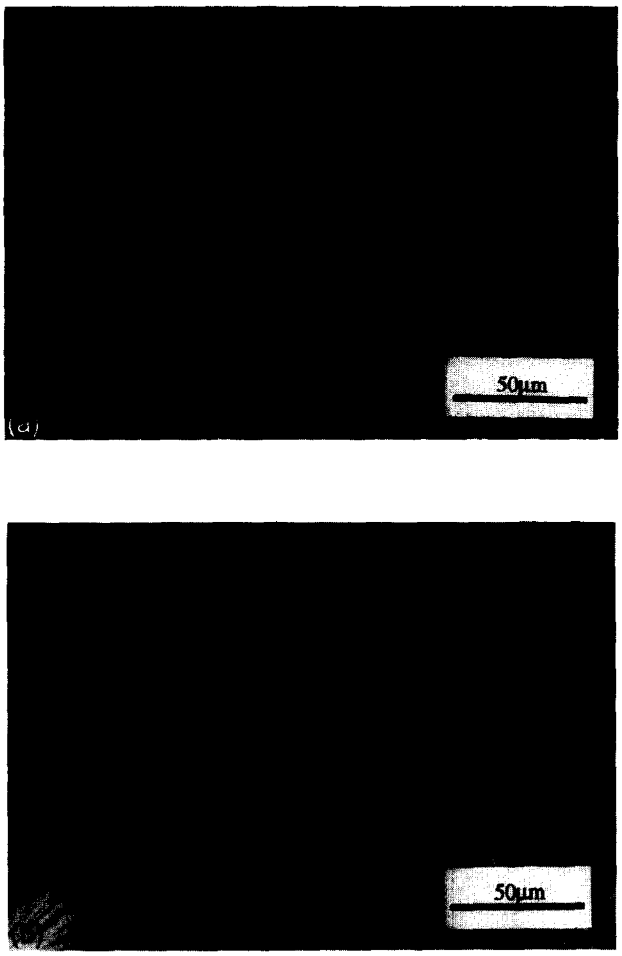

Figure 3 Transmission optical micrograph (crossed polars) showing the morphologies that developed close to T_{min}: (a) C294 crystallized at 127°C; (b) C246 crystallized at 123°C

Table 1 Comparison of melting temperatures obtained in this study by hot-stage optical microscopy with published data

Material	Microscopy T_m (°C)	Literature T_m (°C)	Method (ref.)
$C_{192}H_{386}$		127.5	D.s.c. extrapolation[10]
$C_{198}H_{398}$	126.2–126.3	126.6 ± 0.3	D.s.c. direct[3]
$C_{216}H_{434}$		128.4	D.s.c. extrapolation[20]
$C_{246}H_{494}$	128.6–128.7	128.6 ± 0.3	D.s.c. direct[3]
$C_{294}H_{590}$	130.1–130.2	130.4 ± 0.3	D.s.c. direct[3]

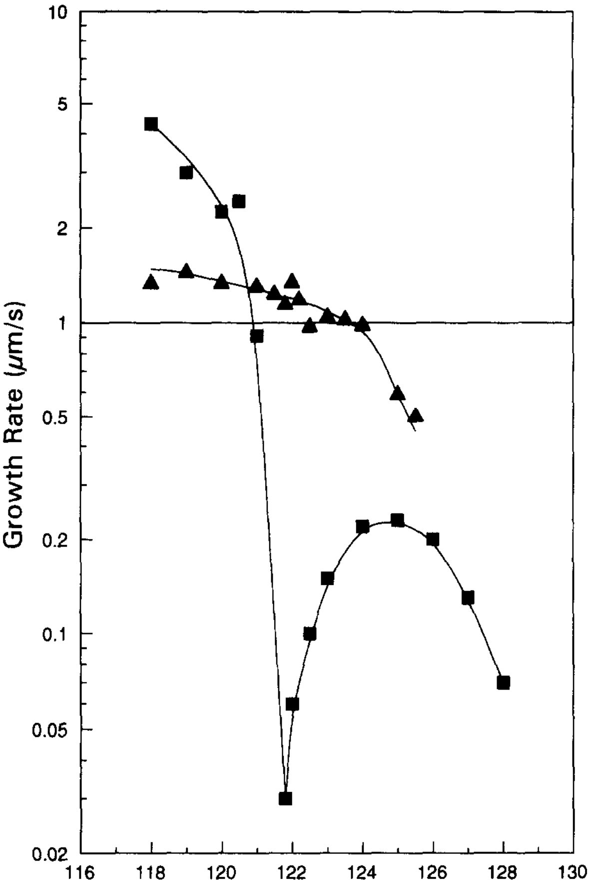

Figure 4 Variation in the crystal growth rate as a function of crystallization temperature for C246 (■) and C198 (▲)

Table 2 Comparison of T_{min} values determined experimentally with T^* values estimated by assuming $T^* = T_{min}$ for C246

Material	Method (ref.)	T_{min} (°C)	T^* (°C)	Origin of T^*
$C_{198}H_{398}$	Microscopy	Not observed	~118	Calculated from $C_{246}H_{494}$
	D.s.c. scan[5]	~116		
$C_{246}H_{494}$	Microscopy	121.8 ± 0.5	121.8	Assumed equal to T_{min}
	D.s.c. isothermal[5]	121.2		
$C_{294}H_{590}$	Microscopy	124.5 ± 0.5	~125	Calculated from $C_{246}H_{494}$

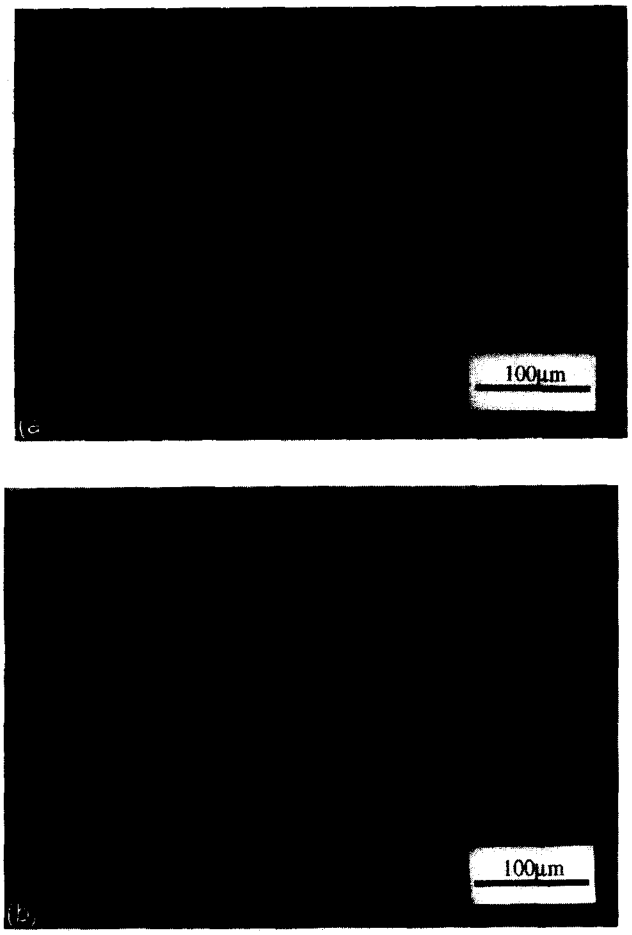

Figure 5 Transmission optical micrographs (crossed polars) showing the range of textures seen in C198: (a) an elliptic polycrystalline aggregate grown at 125.5°C; (b) a coarse, branching texture that developed at 122°C

from solution[6], no growth rate minimum is apparent here. Analogous calculations to those outlined above would suggest a growth rate minimum at $\sim$118°C, whereas dynamic d.s.c. experiments imply a temperature of $\sim$116°C[5]. Such temperatures are inaccessible to us and consequently we have no direct kinetic evidence for a transition from the chain-extended growth that occurs at high crystallization temperatures (TEM data[21]) to chain-folded growth in C198. However, as shown in *Figure 5*, the morphological variations seen in C198 mirror those described above for C294 and C246 and, therefore, it is possible that some change in molecular conformation does occur at lower temperatures*.

Conclusions

The crystallization behaviour of three monodisperse polyethylene oligomers has been described as a function of molecular length and of crystallization temperature. In all three systems, the observed morphologies change systematically with temperature. At high temperatures, coarse lamellar aggregates are formed, which, despite being composed of lamellae that are elliptic in habit (like polyethylene), do not reveal evidence of the branching and splaying processes that are so characteristic of macromolecules. At lower temperatures, spherulitic morphologies have been observed. In C294 and C246, this change is associated with the onset of chain folding, which is accompanied by a marked reduction in crystal growth rates. In the vicinity of the growth rate minimum, chain-extended and chain-folded crystals develop side-by-side. The kinetic behaviour of C198 appears significantly different. Despite similar variations in morphology, no minimum in crystal growth rate has been observed in the temperature range that is accessible to us.

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*This conclusion is, however, at odds with as yet unpublished results that have recently been brought to our attention[22]. This apparent contradiction will be discussed fully in a subsequent publication[21]