ELSEVIER

Polymer 41 (2000) 1953–1957

polymer

Polymer Communication

The crystallization kinetics of monodisperse $C_{98}H_{198}$ from the melt

J. Teckoe, D.C. Bassett*

J.J. Thomson Physical Laboratory, The University of Reading, Whiteknights, Reading RG6 6AF, UK

Received 24 February 1999; received in revised form 8 July 1999; accepted 12 July 1999

Abstract

The crystallization kinetics of the monodisperse *n*-alkane $C_{98}H_{198}$, growing as extended-chain lamellae from the melt, have been measured as part of a wider programme on these novel model systems for polymeric materials. Crystal growth rates decrease linearly, by a factor of 30, over the temperature range of 113.5–114.9°C, an interval which encompasses a significant change in habit from individual through parallel-stacked lamellae to a type of coarse spherulite. The data differ considerably in character from those reported previously for extended chain crystallization of *n*-$C_{198}H_{398}$ but are comparable to earlier studies of purified *n*-$C_{94}H_{190}$ and are sensibly linear with supercooling as proposed in Hoffman's theory of extended-chain crystallization. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Crystallization kinetics; Monodisperse *n*-alkanes; Extended-chains

1. Introduction

The monodisperse *n*-alkanes are members of a family of polyethylene oligomers synthesized so as to give no detectable homologues [1,2]. They are of special interest as model systems whose precision may help clarify issues of polymeric crystallization independent of polydispersity. Of particular note is that these *n*-alkanes tend to form lamellae of quantized thicknesses with the end groups confined to the basal lamellar surfaces [3]. Although several states have been reported for sufficiently long molecules crystallized from solution, for melt growth the common situation for *n*-alkanes with from ~200 to ~400 C atoms in the chain is for only extended and once-folded conformations to occur, the former nearer to the melting point. Shorter molecules, with lengths decreasing towards ~10 nm, give just the extended form.

This bimodal situation can be reflected by the growth kinetics showing a minimum with temperature where one form gives way to the other [4,5], a phenomenon which is widely attributed to mutual interference of the two conformers at the growth front, so-called 'self-poisoning' [6]. It is also evidenced in the morphology, with the dominant/subsidiary microstructure characteristic of polymer spherulites present when there is folding and absent when there is none [7,8]. The kinetics are not, however, always so clear cut. Whereas both *n*-$C_{294}H_{590}$ and *n*-$C_{246}H_{494}$ do show well-defined minima, none was observed for *n*-$C_{198}H_{398}$ at least over the attainable 8 K isothermal temperature interval [5]. Under these conditions, SAXS and electron microscopy showed that crystallization of *n*-$C_{198}H_{398}$ was still in the extended form [9]. As, however, both these techniques also showed that the once-folded form is produced on quenching [9] it is conceivable that the interference of embryonic folding is relevant to the kinetics which show only a very small (threefold) variation in crystallization rate across the accessible 8K temperature interval and differ from Hoffman's theory of extended-chain crystallization [10] in that the rate is not linear with supercooling.

The work of this note has extended the range of *n*-alkanes investigated to *n*-$C_{98}H_{198}$ which can only crystallize in the extended form and for which self-poisoning by an alternative quantized state will not be a factor. While the process of extended-chain growth is likely to involve stages of partial attachment when the wrong conformation could possibly delay growth in a similar way to models proposed by Sadler for polymeric crystallization [11,12] it has been concluded that, in practice, this is not a significant factor for the *n*-alkanes [10]. We find that for this paraffin the growth rate varies by ~30 over the measured crystallization range which was only 1.4 K wide. Within this region the variation of growth rate is sensibly linear with supercooling in agreement with Hoffman's theory of extended-chain growth. At the same time there is a hint of non-linearity when the gross morphology changes from single crystal/lamellar aggregates to more spherulitic forms. These two factors raise the question of whether or not partial attachment of chains to a growing lamella is significant in generating a diverging

---

* Corresponding author.

0032-3861/00/$ - see front matter © 1999 Elsevier Science Ltd. All rights reserved.
PII: S0032-3861(99)00467-X

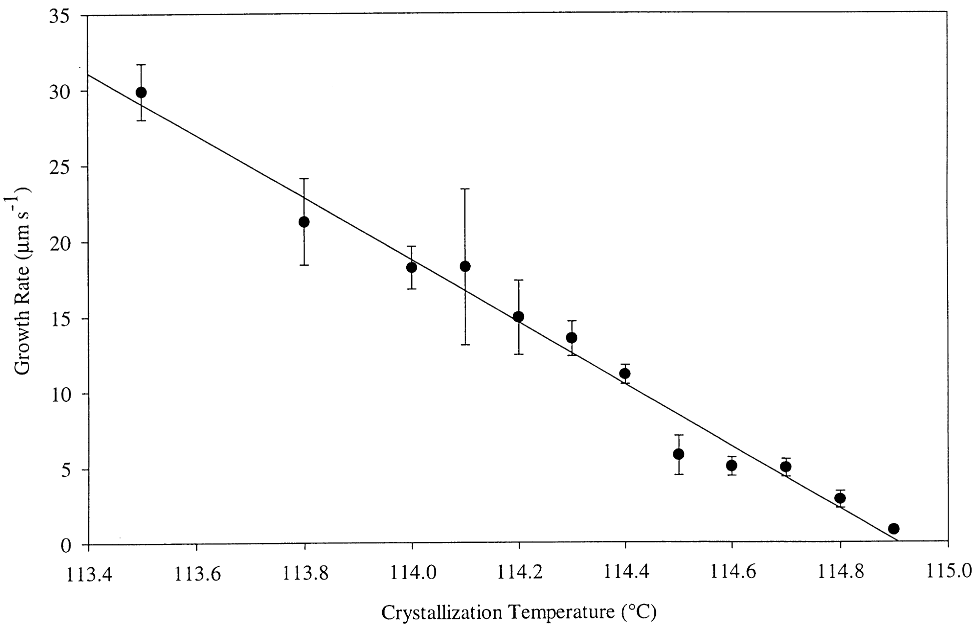

Fig. 1. Graph of growth rate vs crystallization temperature for n-$C_{98}H_{198}$.

morphology even though it may not be the rate-controlling step for the kinetics.

2. Experimental

The monodisperse n-alkane, $C_{98}H_{198}$ was kindly provided by Dr G. M. Brooke, University of Durham, under the auspices of the EPSRC. Samples were crystallized between slide and cover slip after melting at 120°C for some seconds. For isothermal experiments they were cooled, under oxygen-free nitrogen in a Mettler hot stage, from 120°C to the required crystallization temperature at a rate of 10 $K.min^{-1}$. Growth rate data were calculated by capturing successive images in a polarizing microscope using a CCD camera and video recorder. The maximum (long-axis) dimensions, typically of ~20 but on occasion as many as 47, crystals were monitored with time at a number of

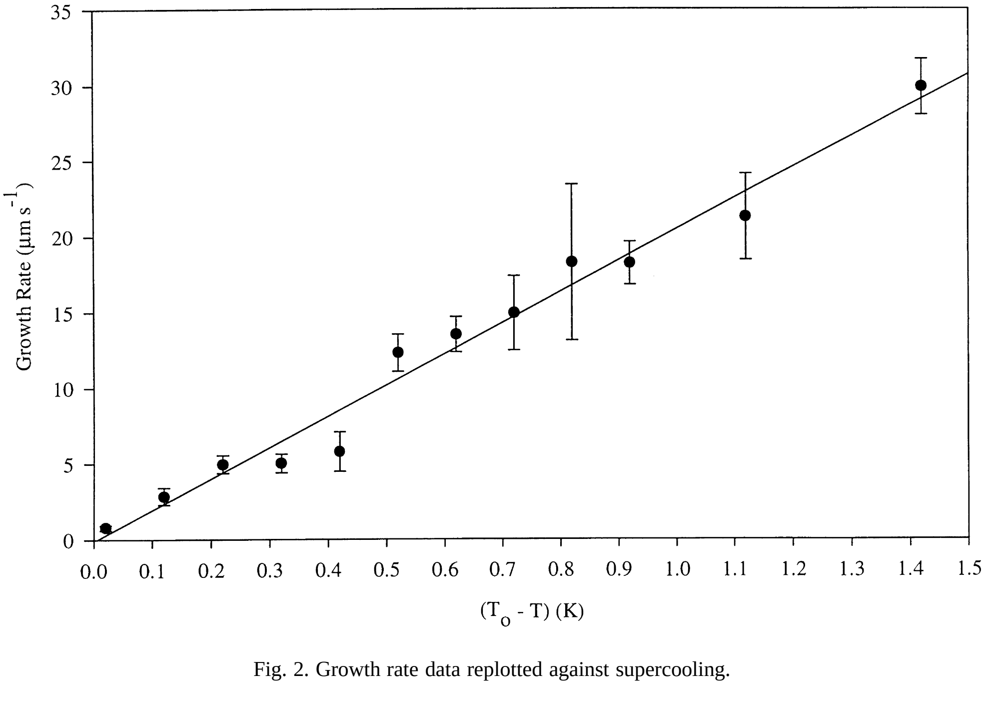

Fig. 2. Growth rate data replotted against supercooling.

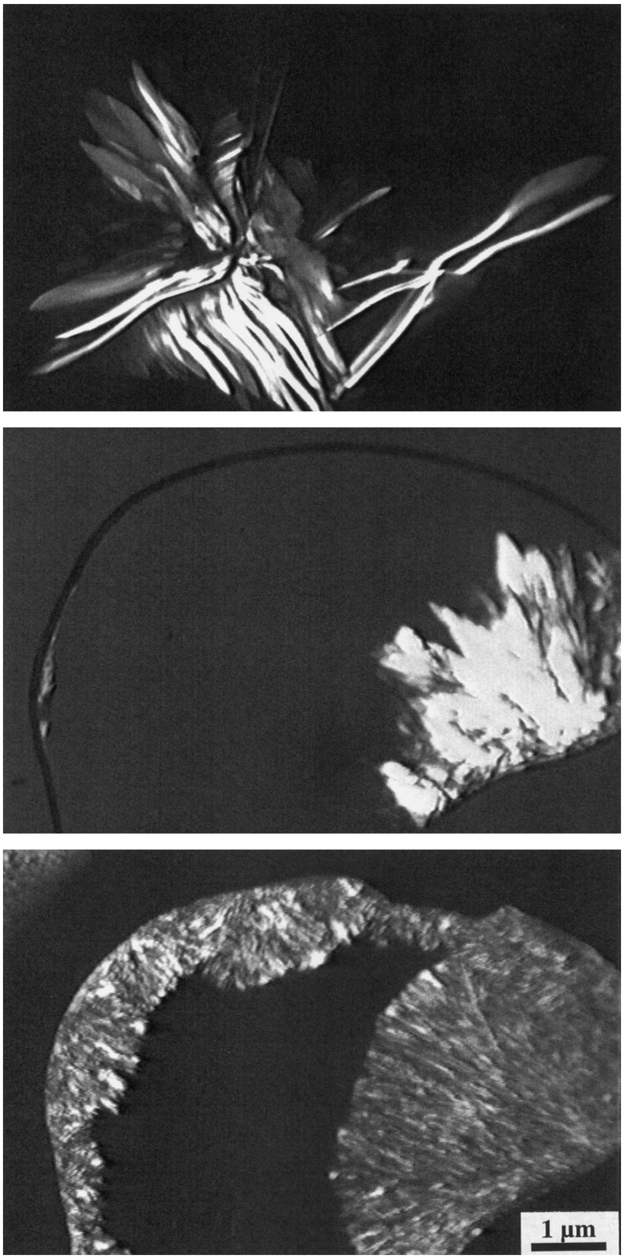

Fig. 3. Polarizing optical micrographs of $C_{98}H_{198}$ crystallized at 115.6, 115.5 and 113.8°C, from top to bottom, respectively.

crystallization temperatures then converted into (linear) growth rates. There was no sign that samples had suffered any degradation during the crystallization procedure; uniformity of appearance was maintained to the edge of the cover slip.

3. Results

Growth rate data accumulated for monodisperse n-$C_{98}H_{198}$ in the temperature range 113.5°C – 115.9°C are presented in Fig. 1 When the data of Fig. 1 are replotted in the form of Hoffman's equation [10]

$$G = K(T_0 - T)$$

they appear as in Fig. 2 and are sensibly linear as predicted. Here the value of T_0, the melting temperature of this paraffin, has been taken to be 114.95°C, a figure derived by interpolation of numerical data of Broadhurst [14]. In consequence the value of the constant K, the slope of Fig. 2, for n-$C_{98}H_{198}$ is evaluated as $2.05 \times 10^{-3}\,\mathrm{cm\,s^{-1}\,K^{-1}}$. This value is ~4 times greater than for the previous data [10] for purified n-$C_{94}H_{190}$ which, in the context of crystal growth, may be regarded as not unsatisfactory agreement.

The data are consistent with the least squares line shown, although there is a hint that two points, those for $\Delta T = 0.45$ and 0.35 K (114.5 and 114.6°C), may fall just below it and similarly in Fig. 1. In both instances, however, the shortfall is two standard deviations (of the respective populations), i.e. the 95% confidence limit is not exceeded, so the deviations can not be regarded as strongly significant on the basis of the data reported here. As in previous work on n-alkane kinetics [5] there does appear to be an inherent variability in behaviour so that more measurements do not markedly reduce the variance of the population. Nevertheless, subsequent work [13] has found similar deviations in the kinetics of extended-chain growth for the C_{122}, C_{162} and C_{246} n-alkanes. In all cases this coincides with a change in habit, for increasing supercooling, from single crystal/lamellar aggregates to branching and a form of coarse spherulite as shown in Fig. 3. It does appear, therefore, that our observations have revealed a new phenomenon of some consequence.

4. Discussion

The principal conclusion of this note is that the kinetics of purely extended-chain growth in n-$C_{98}H_{198}$ differ qualitatively from those of n-$C_{198}H_{398}$ growing as extended chains [5] and are in agreement with the prediction of Hoffman's theory [10].For the latter alkane the once-folded state does exist, albeit for crystallization at temperatures below those attainable for isothermal growth. No minimum in isothermal growth was observed but, knowing that the once-folded form is attainable by quenching [9], it is not unreasonable to assume that a minimum may exist at an isothermally unattainable lower temperature. In so far as the slowing of kinetics in n-$C_{198}H_{398}$ may be attributed to 'self-poisoning', i.e. the wrong molecular conformation (folding) being present at the interface of the extended-chain lamella hindering its growth [4,6], partial attachment of stems to the interface should be expected. This accords with statistical thermodynamics which teaches that all configurations of a system will be explored, as will be true also of n-$C_{98}H_{198}$.

Although partial attachment has been inferred not to be the rate-controlling step in extended-chain crystallization

[10] this does not exclude it having a possible role in determining the morphology. This matter arises principally because of the strong correlation of spherulitic microstructure with folding reported [7,8] for n-$C_{294}H_{590}$ in confirmation of suggestions emanating from the characteristic dominant/subsidiary microstructure of polymeric spherulites [15]. Their spherical geometry with crystallographically equivalent radii derives from adjacent dominant lamellae splaying apart at branch points by near constant angles $\sim 20°$ with distortion of what are very flexible lamellae confined to a small region for which lamellar separations are no greater than the molecular length [16]. This is not a nucleation effect but a distortion as is most clearly seen by the divergence of successive layers of a spiral terrace around a giant screw dislocation in one crystal [17]. A mesoscopically short-range repulsive force effective only within a molecular length must, therefore, operate between adjacent dominant lamellae during growth.

The suggestion made following the early systematic electron microscopic studies [18,19], was that this force was likely to result from the pressure of dynamic cilia during growth. The monodisperse n-alkanes presented the first simple means of testing this proposal because of their tendency to crystallize with quantized thicknesses with end groups confined to basal surfaces. Accordingly, there should be a marked difference between crystallization of extended and chainfolded molecular conformations. Dynamic ciliation will be greater for the latter because in the deposition of a once-folded molecule there is liable to be a stage when only half the molecule is attached with the remainder occupying space outside the lamella and able to resist any competition for that space by a developing neighbouring lamella with a weak rubbery modulus. There is indeed a striking correlation of changed microstructure with molecular conformation as was demonstrated for n-$C_{294}H_{590}$ with diverging dominant lamellae and spherulitic growth present for once-folded growth but absent for extended-chain crystallization [7,8]. The latter has a texture of parallel lamellae, as is also present in published micrographs [20] of n-$C_{94}H_{190}$. The dominant/subsidiary microstructure of n-$C_{294}H_{590}$ in the once-folded form implies that a repulsive force must operate over a range at least one order of magnitude less than could be inferred for polymeric spherulites. Its range in paraffins can be no more than several nm and will, therefore, only operate very close to the branch point when a developing lamella is very small. Under these circumstances cilia emanating from side surfaces will be close to the branch point and exercise comparatively greater influence on development than for larger dimensions.

Further experiments [21] adding small amounts of monodisperse molecules, either shorter or longer, to n-$C_{122}H_{246}$ crystallizing with extended chains as host, have confirmed the principal consequences of dynamic ciliation. The addition of longer and co-crystallizing molecules, which must cause profuse ciliation, gave the anticipated fine-textured spherulitic growth and a much reduced growth rate. The addition of shorter molecules at temperatures where they were unable to crystallize gave cellulation within coarse spherulites, accompanying no*n*-linear growth. However, the host polymer did itself show a tendency to solidify as a form of coarse spherulite as crystallization temperatures decreased. The observations [20] on n-$C_{94}H_{190}$ reported similar behaviour and also a microstructure of parallel lamellae similar to that found for the extended-chain growth in n-$C_{294}H_{590}$.

An apparent paradox results in that there is strong experimental support [15] for the characteristic dominant/subsidiary microstructure of polymeric and paraffinic spherulites being a consequence of dynamic ciliation. On the other hand there is the question of how the spherulites formed by extended-chain crystallization are to be explained if molecules add as complete stems and there is no ciliation. These spherulites appear to be subject to a weaker randomisation process than polymer spherulites, tending to lack their fine textures with equivalent radii but optically showing single-crystalline orientations over broad arcs such as might have been established in primary nucleation. Nevertheless they do show systematic splaying apart of successive units [13] again implying that a short-range repulsive force is at work. It is conceivable that this might result from transient ciliation due to the difference between the thickness of the extended nucleus, ℓ, and the molecular length, L. One may estimate this as

$$(L - \ell) \sim L(1 - \Delta T_0/\Delta T)$$

for a supercooling ΔT in relation to the minimum supercooling ΔT_0 for finite growth rate because the free energy of crystallization is proportional to supercooling. If we take the estimate [10] of $\Delta T_0 = 0.039$ K for n-$C_{94}H_{190}$ as a guide it is clear that the distances $(\mathrm{L} - \ell)$ involved can be a considerable fraction of the molecular length and, as such, begin to approach the fold length of the higher n-alkanes such as n-$C_{198}H_{398}$.

These aspects of the crystallization of the monodisperse n-alkanes are of considerable interest with significant implications for polymers. We have, accordingly, embarked upon a morphological study of n-$C_{98}H_{198}$ in parallel with the above work to establish the relevant microstructures and help resolve the fundamental issues.

Acknowledgements

This worked was funded by EPSRC as part of its programme on monodisperse n-alkanes.

References

[1] Paynter OI, Simmonds DJ, Whiting MC. The synthesis of long-chain unbranched aliphatic compounds by molecular doubling. J Chem Soc Chem Commun 1982;1175–1176.

[2] Bidd I, Holdup DW, Whiting MC. Studies on the synthesis of linear aliphatic compounds. Part 3 The synthesis of paraffins with very long chains. J Chem Soc Perkin Trans 1987;1:2455–2463.

[3] Ungar G, Stejny J, Keller A, Bidd I, Whiting MC. The crystallization of ultralong normal paraffins: the onset of chain folding. Science 1985;229:386–389.

[4] Ungar G, Keller A. Inversion of the temperature dependence of crystallization rates due to chainfolding. Polymer 1987;28:1899–1907.

[5] Sutton SJ, Vaughan AS, Bassett DC. On the morphology and crystallization kinetics of monodisperse polyethylene oligomers crystallized from the melt. Polymer 1996;37:5735–5738.

[6] Higgs PJ, Ungar G. The growth of polymer crystals at the transition from extended chains to folded chains. J Chem Phys 1994;100:640–648.

[7] Bassett DC, Olley RH, Sutton SJ, Vaughan AS. On spherulitic growth in a monodisperse paraffin. Macromolecules 1996;29:1852–1853.

[8] Bassett DC, Olley RH, Sutton SJ, Vaughan AS. On chain conformations and spherulitic growth in monodisperse n-$C_{294}H_{590}$. Polymer 1996;37:4993–4997.

[9] White HM, Bassett DC. Unpublished work.

[10] Hoffman JD. Growth rate of extended-chain crystals: the lateral surface free energy of pure n-$C_{94}H_{190}$ and a fraction $\sim C_{218}H_{417}$. Macromolecules 1985;18:772–786.

[11] Sadler DM. New explanation for chain folding in polymers. Nature 1987;326:174–177.

[12] Sadler DM, Gilmer GH. A model for chain folding in polymer crystals: rough growth faces are consistent with the observed growth rates. Polymer 1984;25:1446–1452.

[13] Hosier IL, Bassett DC. Presented at ACS conference, New Orleans, August 1999; submitted to Polymer.

[14] Broadhurst MG. An analysis of the solid phase behavior of the normal paraffins. J Res NBS 1962;66A:241–249.

[15] Bassett DC. Lamellae and their organization in melt-crystallized polymers. Phil Trans R Soc A 1994;348:29–43.

[16] Patel D, Bassett DC. On spherulitic crystallization and the morphology of melt-crystallized isotactic poly(4-methylpentene-1). Proc R Soc A 1994;445:577–595.

[17] Bassett DC, Olley RH, al Raheil IAM. On isolated lamellae of melt-crystallized polyethylene. Polymer 1988;29:1539.

[18] Bassett DC, Olley RH. On the lamellar morphology of isotactic polypropylene spherulites. Polymer 1984;25:935–943.

[19] Bassett DC, Vaughan AS. On the lamellar morphology of melt-crystallized isotactic polystyrene. Polymer 1985;26:717–725.

[20] Khoury F. Crystal habits and morphology of n-tetranonacontane (n-$C_{94}H_{190}$). J Appl Phys 1963;34:73–79.

[21] Hosier IL, Vaughan AS, Bassett DC. Unpublished work.