ELSEVIER

Polymer 43 (2002) 5979–5984

polymer

www.elsevier.com/locate/polymer

# The occurrence of hexagonal phases in three monodisperse long *n*-alkanes at high pressures

I.L. Hosier, D.C. Bassett*

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

Received 20 May 2002; received in revised form 19 July 2002; accepted 19 July 2002

**Abstract**

Stable hexagonal phases have been identified in the three monodisperse long *n*-alkanes $C_{390}H_{782}$, $C_{294}H_{590}$ and $C_{246}H_{494}$ at pressures ~0.5 GPa and above. Their isobaric temperature range of stability widens with increasing pressure but decreases for shorter molecular lengths. Crystallization of hexagonal phases from the melt, often under metastable conditions and below the triple point, gives a characteristic morphology distinct from direct crystallization of the orthorhombic phase, as found for polyethylene. The data extend the known stability range of this two-dimensionally ordered phase to shorter molecules and complement previous work on polyethylene and short alkanes. © 2002 Elsevier Science Ltd. All rights reserved.

*Keywords:* Monodisperse *n*-alkanes; Hexagonal phase; High pressure

## 1. Introduction

The high pressure phase of polyethylene is two-dimensionally ordered with hexagonal packing of chains but lacks order along molecules which do not have the all-*trans* conformation of the orthorhombic form [1]. Its crystallization from the melt produces, so-called chain-extended lamellae at lower supercoolings, strikingly thicker [2] than those from the usual crystallization of the orthorhombic phase at higher supercoolings. Its existence was first inferred from morphology and thermodynamic data [3–6] then confirmed by X-ray diffraction at high pressures which also validated the correlation of the characteristic morphology with crystallization into the hexagonal phase [1]. In fact 'chain-extended' lamellae are circular as formed [7] unlike crystals formed in the orthorhombic phase, and present strong birefringence contrast when viewed edge-on in the polarizing microscope. This contrast is mostly lost abruptly in the ensuing first order transition to the orthorhombic phase—which it identifies—occurring on or before return to ambient conditions, when molecules tilt through 35° about the *b*-axis [8].

The phase diagram shows the area of stability for the hexagonal phase widening with pressure in contrast to that for the hexagonal or rotator phases of the short *n*-alkanes, which decreases and eventually disappears with increasing pressure [9,10]. This dichotomy corresponds, in thermodynamic terms, to the difference between phases of high entropy and high volume, inviting the question of what molecular length is required to effect the change of pattern.

Previous work showed [11] that the isobaric stability range of the hexagonal phase decreased for shorter molecules down to ~$10^4$ in molecular weight. Moreover, solvent extraction of the lower end of the molecular distribution from commercial polyethylenes avoided segregation of low melting populations on crystallization at ~0.5 GPa which were a major cause of brittleness and were suggested not to have entered the hexagonal phase [12]. Molecular length measurements, by GPC, of such populations after selective extraction, gave ~60 nm average chain length (~6600 molecular mass) as the lower limit to enter the high-pressure phase at ~0.5 GPa [13]. In a more detailed study, Asahi found [14] that fractions of 1000 and 2000 molecular mass did not show the high pressure phase to ~1 GPa but those of 6500 and above did. We now report the complementary observations of a high pressure phase in three monodisperse *n*-alkanes: $C_{390}H_{782}$ ($M_m = 5462$), $C_{294}H_{590}$ ($M_m = 4118$) and $C_{246}H_{494}$ ($M_m = 3446$). So far as we are aware, *n*-$C_{246}H_{494}$ is the shortest *n*-alkane in which the high-pressure hexagonal phase has so far been

---

* Corresponding author. Tel.: +44-118-931-8540; fax: +44-118-975-0203.

*E-mail address:* d.c.bassett@reading.ac.uk (D.C. Bassett).

PII: S0032-3861(02)00503-7

reported. Increasing length favours formation of the high-pressure phase because of the increased entropy it brings, presumably from conformational disorder along the chain.

## 2. Experimental

### 2.1. Nomenclature

The three monodisperse *n*-alkanes $C_{390}H_{782}$, $C_{294}H_{590}$, $C_{246}H_{494}$, used in this work were all synthesized and supplied by Dr GM Brooke and colleagues at the University of Durham, following Whiting [15,16], under the auspices of EPSRC. For convenience these will hereafter be denoted C390, C294 and C246, respectively.

### 2.2. High pressure DTA

High-pressure differential thermal analysis, DTA, experiments were undertaken using a piston-cylinder press as previously [17] but with a modified cell. In this, the sample and a PTFE reference (each ~10 mg) were wrapped separately in aluminium foil prior to insertion into a specially constructed high pressure DTA cell for which pressure was calibrated against the melting of high purity indium as standard. DTA heating scans were performed at a series of constant pressures from 0.1 to 0.8 GPa, with scan rates ranging from 2 K $\text{min}^{-1}$ at the lowest temperatures to 0.5 K $\text{min}^{-1}$ at the highest temperatures, these being limited by the thermal mass of the press and its heat losses. The DTA signal was amplified with a gain of 100 by a Linear Technology LT1050 chopper stabilized amplifier, with low pass filtering centred at 0.3 Hz, before being fed to a Keithley Model 181 Nanovoltmeter. Simultaneously the sample temperature was registered on an electronic thermocouple display to an accuracy of ±1 K. The DTA signal plotted against temperature allowed the peak values of endothermic transitions to be determined reproducibly.

### 2.3. Diamond anvil cell (DAC)

Samples of the required *n*-alkane were placed in a hole, 0.6 mm in diameter, bored in a 50 μm thick sheet of nickel alloy and melted gently on a Kofler WME hot-bench so as to form a continuous film inside the hole. The sheet with sample was inserted between parallel diamonds of a gasketed DAC to the design of Barnett et al. [18] and fitted with an external heater, similar to that on which the X-ray pattern of the high pressure phase was first recorded [1]. With the hole centred optically, a moderate pressure was applied, at ambient temperature, so as to hold the sample tightly in place and the entire assembly mounted on the stage of a Vickers Universal Microscope, allowing crystallization to be observed in situ and photographed through the diamonds. For each experiment a fresh sample of the required *n*-alkane was prepared in a fresh gasket and the diamonds scrupulously cleaned to avoid cross-contamination of these ultra-pure materials. The scale of the microscope was calibrated using a standard graticule at room temperature.

It is not possible to measure the pressure sufficiently precisely directly in the DAC, however, previous experience in using devices of this type to study the crystallization of polyethylene [1] has shown that the most sensitive and reliable measure of pressure in the cell is the final melting point. Data from this laboratory exist for linear polyethylene up to pressures of 0.6 GPa ($T_m = 263$ °C) which are now supplemented by our DTA data for all three *n*-alkanes, whose melting points are less than polyethylene at any given pressure, and extrapolations therefrom. In the gasketed DAC it should be noted that the pressure falls as crystallization proceeds because it operates essentially at constant volume with the constant load sustained by the gasket, thereby widening the temperature range over which transitions occur [1]. Consequently, quoted pressures for the DAC correspond to *nominal* pressures obtained on melting the cell contents.

### 2.4. Stability of the hexagonal phase

Although the hexagonal phase of polyethylene often crystallizes in a metastable condition at finite supercoolings [6], its thermodynamic stability in relation to the phase diagram can be assessed on re-melting because there is little or no superheating on melting due to the presence of suitable nuclei. Accordingly, the presence or absence in DTA data of the two successive first-order transitions from orthorhombic to hexagonal to melt indicates whether the hexagonal phase is, or is not, stable under the operating pressure.

In the DAC an equivalent test is reproduction of the original hexagonal texture, with strong birefringence, on reheating the specimen. If the original clear texture is reproduced then the hexagonal phase is said to be stable (at that pressure) but if not, the hexagonal phase is said to be metastable.

### 2.5. Experimental procedure

Experiments in the DAC were performed at pressures for which the alkane melting point was between 190 and 290 °C. Temperatures higher than this were not used, seeking to avoid possible degradation and cross-linking. For pressures much less than that required to give a melting point of 190 °C, the sealing of the gasket was liable to be poor resulting in leakage of the contents. Nominal melting points of 200, 230, 250, 265 and 280 °C were, therefore, chosen within this working range to give a useful range of accessible pressures.

To set a desired pressure in the DAC, the following procedure was adopted. The specimen was first melted at 145 °C, the pressure increased by a small amount both to

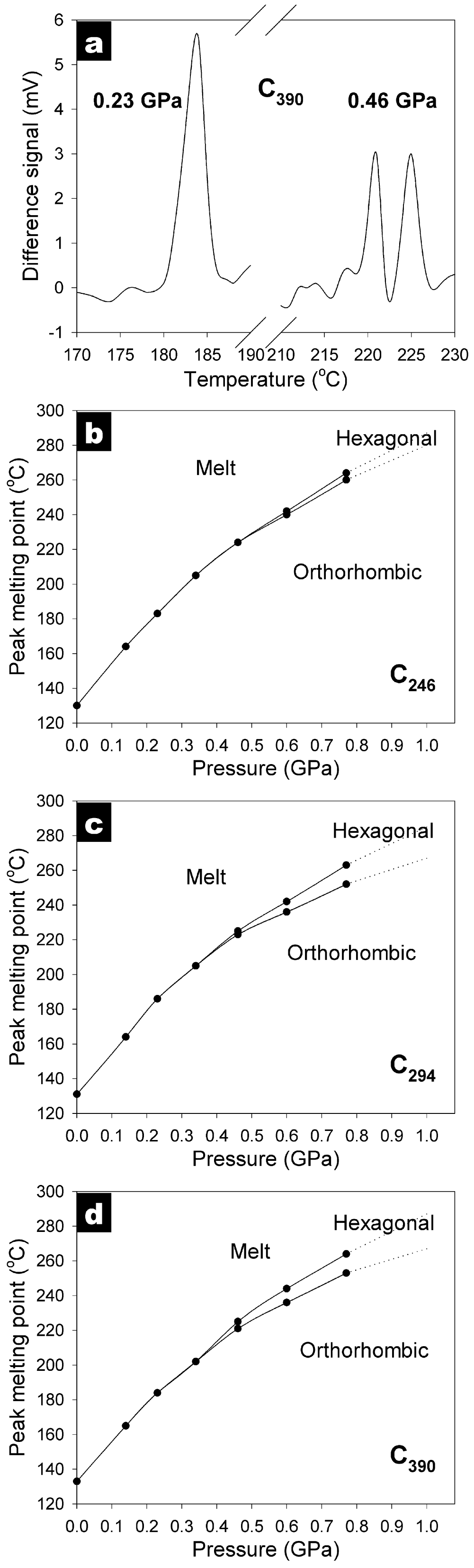

Fig. 1. Results from high-pressure DTA experiments: (a) sample of DTA data from C390; phase diagrams for (b) C246, (c) C294, (d) C390.

induce immediate crystallization and to prevent leakage, then the melting point at the new pressure was determined optically. This was compared to the melting temperature required and the load adjusted accordingly. After cooling and allowing the sample to crystallize at this new pressure, the new melting point was determined and the procedure repeated as necessary until the melting point was within 10 K of that wanted.

The experiment proper was performed, at constant load, as follows: the temperature was raised 10 K above the initial melting temperature ($T_i$) to melt the specimen completely. The temperature was then reduced to 15 K below $T_i$ and held there to nucleate and begin to crystallize. When the consequent morphological changes were complete, a photograph was recorded. It was then reduced similarly, in 10 K steps, to 150 °C with a photograph taken at each stage. An equivalent procedure was adopted as the sample was reheated from 150 °C, in 20 K steps, to the melting temperature. For a run to be acceptable this final melting temperature, $T_f$, had to be essentially the same as that measured initially.

## 3. Results

### 3.1. Phase behaviour

An example of the raw DTA data from the experiments is plotted in Fig. 1a. At low pressures only a single DTA peak was observed corresponding to the melting of crystals in the normal orthorhombic phase. At higher pressures a double peak is obtained, the first feature being associated with the orthorhombic to hexagonal transition and the second due to the melting of the crystals hence formed. This information allows the phase diagrams shown in Fig. 1b–d to be plotted for each material in turn and the hexagonal stable region to be determined with some certainty. The upper (melting) phase line allows the melting points from the DAC to be used to calculate the nominal cell pressure. For each pure alkane the position of this melting line was very similar, lying below that for polyethylene (2,3)—with significant depression at high pressures. The phase diagram for C246 shows a very narrow hexagonal region (Fig. 1b), whereas those of C294 (Fig. 1c), and C390 (Fig. 1d), are rather similar and broader.

The comparable results from the DAC experiments are summarised in Table 1. This table indicates the melting points $T_i$, $T_f$ and the calculated nominal cell pressure $P_{NOM}$. One of three behavioural patterns was experienced depending on sample and pressure denoted O, M or H: O implies that orthorhombic crystals formed at all temperatures at this pressure; M is when the hexagonal phase crystallized in a metastable condition but did not reform on heating; H indicates that the hexagonal phase is stable occurring between orthorhombic and melt phases during both crystallization and melting sequences.

Table 1
High pressure melting and crystallization data

| Material | $P_{NOM}$ (GPa) | $T_i$ (°C) | $T_f$ (°C) | Phase | $T_1$ (°C) | $T_2$ (°C) |
|---|---|---|---|---|---|---|
| C246 | 0.31 ± 0.01 | 200 | 205 | O | – | – |
| | 0.52 ± 0.01 | 230 | 235 | O | – | – |
| | 0.70 ± 0.01 | 255 | 255 | M | 240 | 220 |
| | 0.88 ± 0.02 | 275 | 275 | M | 260 | 230 |
| | 1.01 ± 0.04 | 290 | 290 | H | 270 | 240 |
| | 0.92 ± 0.04 | 280 | 280 | H | 260 | 230 |
| C294 | 0.27 ± 0.01 | 195 | 195 | O | – | – |
| | 0.46 ± 0.01 | 225 | 230 | M | 210 | 180 |
| | 0.67 ± 0.02 | 250 | 255 | H | 230 | 200 |
| | 0.76 ± 0.02 | 260 | 270 | H | 240 | 210 |
| | 0.95 ± 0.04 | 280 | 280 | H | 250 | 210 |
| | 1.00 ± 0.05 | 285 | 290 | H | 260 | 220 |
| C390 | 0.32 ± 0.01 | 195 | 205 | O | – | – |
| | 0.46 ± 0.01 | 225 | 230 | H | 210 | 180 |
| | 0.68 ± 0.02 | 250 | 260 | H | 230 | 200 |
| | 0.83 ± 0.03 | 270 | 270 | H | 240 | 210 |
| | 0.95 ± 0.04 | 280 | 275 | H | 250 | 210 |

When hexagonal crystals do form, further cooling causes these to convert to the orthorhombic phase, indicated by the altered birefringence contrast, beginning at temperature $T_1$ and completed at temperature $T_2$. Table 1 shows that the transition temperatures $T_1$ from the DAC data lie close to the lower lines plotted in the phase diagram. The small discrepancy in the values is partly because the DTA data were obtained on heating, whereas the values for $T_1$ are determined on cooling and so occur at finite supercooling, and partly because of the reduction in pressure in the constant volume DAC which crystallization causes. The latter effect is no doubt responsible for the considerable broadening represented by the interval between $T_1$ and $T_2$ as observed previously [1].

### 3.2. Morphology

The details of each alkane's behaviour are discussed below; they are consistent with and confirm the phase diagrams of Fig. 1. Thus at ~0.5 GPa, C246 crystallizes solely in the orthorhombic phase (Fig. 2a) whereas C294 forms a metastable hexagonal phase, Fig. 2b, which does not reform on heating (Fig. 2c) in contrast to C390 for which Fig. 2d shows the return of a stable hexagonal phase on reheating.

#### 3.2.1. C390

For a nominal pressure of 0.32 GPa, the crystals formed are orthorhombic with the characteristic 'muddy' texture. This appearance does not change significantly with temperature and was retained throughout reheating.

For a nominal pressure of 0.46 GPa, the crystallized texture is a mixture of hexagonal (distinctive spiky) crystals and a muddy and indistinct orthorhombic phase. However, on further cooling, the morphology exhibits a distinctive change in texture between 210 and 180 °C finally exhibiting the muddy appearance of the orthorhombic phase. On reheating to 220 °C (Fig. 2d) some memory of the spiky crystals remains and although still clearly a mixture of both phases the presence of a proportion of restored hexagonal phase suggests that the alkane is just above its triple point.

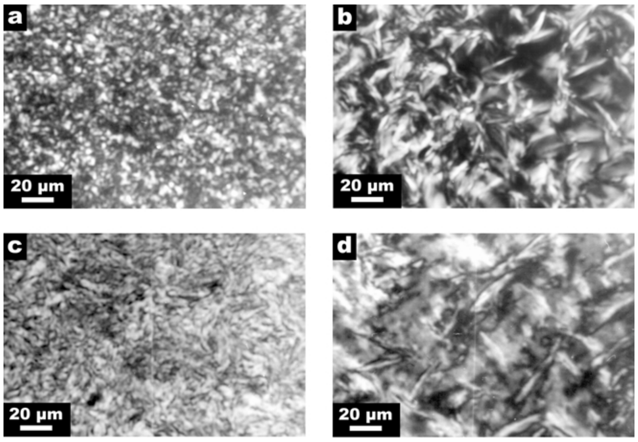

Fig. 2. In situ polarizing optical micrographs recorded with the DAC: (a) C246 crystallized at 0.52 GPa and 220 °C; (b) C294 crystallized at 0.46 GPa and 210 °C; (c) C294 after reheating to 210 °C; (d) C390 crystallized at 0.46 GPa then reheated to 220 °C.

For a nominal pressure of 0.83 GPa, the initial morphology is clearly hexagonal in nature with large isolated crystals apparent at 260 °C these fill space on further cooling and by 200 °C (below $T_1$) the texture is largely muddy and indistinct indicative of a change to the orthorhombic phase but with some evidence of the prior morphology retained. On reheating the original texture is largely restored indicating that the hexagonal phase is stable at this pressure.

#### 3.2.2. C294

For a pressure of 0.27 GPa, a muddy orthorhombic texture forms which does not change on cooling. On reheating a similar texture is retained until the onset of melting. For a pressure of 0.46 GPa, initially a mixture of spiky crystals and more muddy regions forms as for C390 at this pressure (Fig. 2b). Below $T_1$, the texture reverts to the muddy appearance of the orthorhombic phase, which is then retained on further cooling. On reheating, the spiky crystals are not reproduced (Fig. 2c) and this phase subsequently melts directly. Clearly such hexagonal crystals are metastable in nature forming on crystallization at this pressure but not being recovered on heating.

For pressures ~0.6 GPa and above, a stable hexagonal phase forms. The texture of initially hexagonal crystals which forms at 0.67 GPa and 240 °C is retained, albeit with some additional space filling, to ~230 °C (just above $T_1$), but the sample appears completely orthorhombic below ~200 °C. The disrupted internal contrast of lamellae due to the hexagonal to orthorhombic transition can be seen at 220 °C. On reheating, the original hexagonal texture is largely restored albeit with some direct melting, hinting at

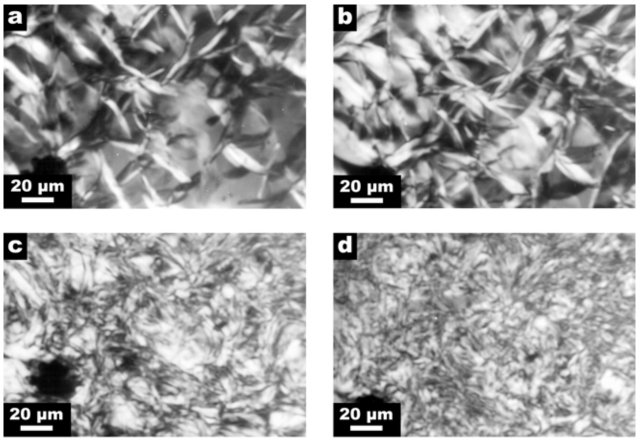

Fig. 3. In situ polarizing optical micrographs recorded with the DAC: C246 crystallized at 0.88 GPa and (a) 270 °C; (b) 260 °C; (c) 240 °C; (d) reheated to 270 °C.

the stability of the hexagonal phase at this and higher pressures.

### 3.2.3. C246

No evidence of the occurrence of the hexagonal phase was found for pressures below ~0.6 GPa as is shown in Fig. 2a for 0.52 GPa pressure. After crystallizing at 220 °C the morphology is clearly orthorhombic and remains so on further cooling and through subsequent reheating. At 0.88 GPa clear evidence of a metastable hexagonal phase is seen, the initial hexagonal phase is much more distinct (Fig. 3a) and becomes space filling at ~260 °C (Fig. 3b) and then is obscured completely below ~240 °C (Fig. 3c); this phase is not recovered on reheating to 270 °C (Fig. 3d) and the orthorhombic phase melts directly.

An example of a stable hexagonal phase in this alkane is shown in Fig. 4a for 1.01 GPa with the initial crystallites of characteristic shape. Space is filled at ~270 °C (Fig. 4b) while at 245 °C this appearance is lost with internal contrast broken up, Fig. 4c. On reheating, the original hexagonal phase is recovered largely intact; compare Fig. 4d with a.

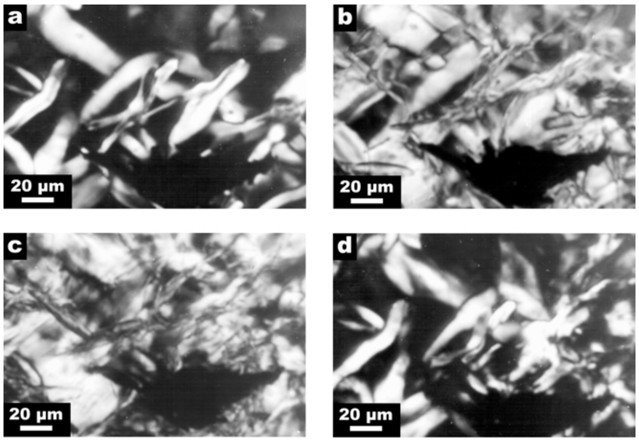

Fig. 4. In situ polarizing optical micrographs recorded with the DAC: C246 crystallized at 1.01 GPa and (a) 280 °C; (b) 270 °C; (c) 240 °C; (d) reheated to 280 °C.

## 4. Discussion

The morphology and DTA behaviour reported here for the three long $n$-alkanes precisely parallel that for linear polyethylene which allowed the inference of the existence of the high pressure phase [3–6]. The endothermic DTA peaks are due to first-order transitions, either a single one from orthorhombic to melt at lower pressures or two successively, from orthorhombic to hexagonal then hexagonal to melt, at higher pressures.[1] The morphology is distinctly different according to the phase to which the melt transformed. The hexagonal phase forms as circular platelets [7] normal to molecules which, viewed edge-on appear with strong birefringence contrast extinguishing when its plane is parallel to either polar [8]. By contrast, crystals form in the orthorhombic phase with habits extended along the $b$-axis in which chains are generally inclined to lamellar normals. Moreover, they do so in a higher, non-overlapping, range of supercooling than does the hexagonal phase [4]. This implies a difference in crystallization rates which leads to the hexagonal phase forming first but metastably, in a zone outside its region of stability in the phase diagram, which can and does extend below the triple point, until the rates of the two competing processes are equal [6]. The discontinuities in supercooling, crystal habit and chain orientation here in the $n$-alkanes and previously in polyethylene do not support claims that the hexagonal phase may always precede the formation of the orthorhombic [19,20]. Possible reasons for the inapplicability of this prediction will be addressed in a subsequent paper.

In thermodynamic terms the hexagonal phase is intermediate in properties, i.e. specific volume and specific entropy, between orthorhombic crystal and isotropic melt. The crystallography shows that it has hexagonal packing of chains in two dimensions but that molecules have more than one conformation along the chain [1]. This will increase the entropy, reduce the free energy and appears to be the underlying reason for the stability of this phase.

The appearance of the hexagonal phase at atmospheric pressure in highly oriented and/or cross-linked polyethylene is because the free energy of the melt is raised due to the entropy of the oriented melt being reduced below that of the unoriented state [17]. In general, once the rise in free energy is sufficient for the orthorhombic melting point to exceed the temperature of the orthorhombic to hexagonal transition, the hexagonal phase will intervene in the melting process. Appropriate endotherms will then show two successive peaks, instead of one, but whose combined normalized area

---

[1] Some combination of the two is possible in the region of the triple point depending on the precise history of the sample.

will, to a first approximation, be unchanged. As explained above, the hexagonal phase will intervene in the crystallization process, metastably, before this condition is precisely attained.

For the long *n*-alkanes, a more appropriate explanation for the appearance and stability of the hexagonal phase may be that its free energy falls, because of increased entropy, once it is possible for the chain to adopt two conformations within its length. Longer molecules would thereby gain more entropy and lower their free energy, which is consistent with the observations of a reduced isobaric range of stability of the hexagonal phase for shorter chains.

## 5. Conclusions

1. Stable hexagonal phases have been identified in the three monodisperse long *n*-alkanes $C_{390}H_{782}$, $C_{294}H_{590}$ and $C_{246}H_{494}$ at pressures ~0.5 GPa and above. Their isobaric temperature range of stability widens with increasing pressure but decreases for shorter molecular lengths.
2. Crystallization of the hexagonal phases from the melt, often under metastable conditions and below the triple point, gives a characteristic morphology distinct from direct crystallization of the orthorhombic phase, as also found for polyethylene.
3. The data extend the known stability range of this two-dimensionally ordered phase to shorter molecules and complement previous work on polyethylene and short alkanes.

## Acknowledgements

This work was funded by EPSRC under whose auspices the monodisperse alkanes used were prepared and supplied by Dr GM Brooke and colleagues at the University of Durham to whom the authors are indebted. Special thanks are due Mr C.J. Balagué for his comprehensive assistance with the experiments using the piston-cylinder press.

## References

[1] Bassett DC, Block S, Piermarini GJ. A high-pressure phase of polyethylene and chain-extended growth. J Appl Phys 1974;45:4146–50.
[2] Geil PH, Anderson FR, Wunderlich B, Arakawa T. Morphology of polyethylene crystallized from the melt under pressure. J Polym Sci A 1964;2:3707–20.
[3] Bassett DC, Khalifa BA, Turner B. Chain-extended crystallization of polyethylene. Nat Phys Sci 1972;239:106–8.
[4] Bassett DC, Turner B. On chainfolded and chain-extended crystallization of polyethylene. Phil Mag 1974;29:285–307.
[5] Bassett DC, Turner B. Chain-extended crystallization of polyethylene: evidence for a new high pressure phase. Nat Phys Sci 1972;240:146–8.
[6] Bassett DC, Turner B. On the phenomenology of chain-extended crystallization in polyethylene. Phil Mag 1974;29:925–55.
[7] DiCorleto JA, Bassett DC. On circular crystals of polyethylene. Polymer 1990;31:1971–7.
[8] Bassett DC. Principles of polymer morphology. Cambridge: Cambridge University Press; 1981. p. 170.
[9] Nelson RR, Webb W, Dixon JA. First order phase transitions of six normal paraffins at elevated pressures. J Chem Phys 1960;33:1756–64.
[10] Wuerflinger A, Schneider GM. High pressure differential thermal analysis. II. Rotational transitions of *n*-alkanes. Ber Bunsenges 1973;77:121–8.
[11] Bassett DC. Chain-extended polyethylene in context: a review. Polymer 1976;17:460–70.
[12] Bassett DC, Carder DR. Oriented chain-extended polyethylene. I. Formation and characterization. Phil Mag 1973;28:513–33.
[13] Olley RH. Unpublished data.
[14] Asahi T. The hexagonal phase and melt of low-molecular-weight polyethylene. J Polym Sci: Phys Ed 1984;22:175–82.
[15] Paynter OI, Simmonds DJ, Whiting MC. The synthesis of long-chain unbranched aliphatic compounds by molecular doubling. J Chem Soc Chem Commun 1982;1165–6.
[16] 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 1 1987;2455–63.
[17] Vaughan AS, Ungar G, Bassett DC, Keller A. On hexagonal phases of paraffins and polyethylene. Polymer 1985;26:726–32.
[18] Barnett JD, Piermarini GJ, Block S. An optical fluorescence system for quantitative pressure measurement in the diamond anvil cell. Rev Sci Inst 1973;44:1–9.
[19] Keller A, Hikosaka M, Rastogi S, Toda A, Barham PJ, Goldbeck-Wood G. The size factor in phase transitions: its role in polymer crystal formation and wider implications. Phil Trans R Soc A 1994;348:3–17.
[20] Keller A, Goldbeck-Wood G. Polymer crystallization fundamentals of structure and crystal growth of flexible chains. In: Aggarval SW, Russo S, editors. Comprehensive polymer science, 2nd Suppl. Oxford: Elsevier; 1996. p. 241–305.