ADVANCES IN POLYMER SCIENCE

180

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Interphases and Mesophases in Polymer Crystallization I

Springer

Interphases and Mesophases in Polymer Crystallization I

Volume Editor: Giuseppe Allegra

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In references Advances in Polymer Science is abbreviated *Adv Polym Sci* and is cited as a journal.

The electronic content of *Adv Polym Sci* may be found at springerlink.com

Library of Congress Control Number: 2005922054

ISSN 0065-3195
ISBN-10 3-540-25345-9 **Springer Berlin Heidelberg New York**
ISBN-13 978-3-540-25345-7 **Springer Berlin Heidelberg New York**
DOI 10.1007/b106919

Springer is a part of Springer Science+Business Media
springeronline.com

Printed in Germany

Cover design: *Design & Production* GmbH, Heidelberg
Typesetting and Production: LE-TEX Jelonek, Schmidt & Vöckler GbR, Leipzig

Printed on acid-free paper 02/3141 YL – 5 4 3 2 1 0

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Preface

Polymer crystallisation is a field of science whose widespread practical and technological implications add to its scientific relevance. Unlike most molecular substances, synthetic polymers consist of long, linear chains usually covering a broad distribution of molecular lengths. It is no surprise that only rarely may they give rise to regularly shaped crystals, if at all. As a rule, especially from the bulk state, polymers solidify as very tiny crystals interspersed in an amorphous matrix and randomly interconnected by disordered chains. How do these crystals form? Do they correspond to a state of thermodynamic equilibrium, or are the chains so inextricably entangled that equilibrium is virtually impossible to reach? There is currently a widespread consensus on the latter conclusion, which only makes the problem more interesting as well as more difficult to handle. The perspective at the base of the present endeavour can be summarised with two questions: What are the key structural steps from the original non-crystalline states to the semi-crystalline organization of the polymer? Do these different stages influence the resulting structure and to what degree?

As demonstrated by the collection of review articles published within three volumes of *Advances in Polymer Science* (Volumes 180, 181 and 191), this problem may be approached from very different sides, just as with the related topic of polymer melting, for that matter. Morphological and atomistic investigations are carried out through the several microscopic and scattering techniques currently available. X-ray, neutron and electron diffraction also provide information to unravel the structure puzzle down to the atomistic level. The same techniques also allow us to explore *kinetic* aspects. The fast development of molecular simulation approaches in the last few decades has given important answers to the many open problems relating to kinetics as well as morphology; in turn, statistical-mechanical studies try to make sense of the many experimental results and related simulations. In spite of several successes over 60 years or more, these studies are still far from providing a complete, unambiguous picture of the problems involved in polymer crystallisation. As one of the authors (an outstanding scientist as well as a very good friend) told me a couple of years ago when we started thinking about this project, we should not regard this book as the solution to our big problem – which it is not – but rather as a sort of "time capsule" left to cleverer and better-equipped scientists of generations to come, who will make polymer crystallisation completely clear.

Thanks to all the authors for making this book possible. Here I cannot help mentioning one of them in particular, Valdo Meille, who helped with planning, suggesting solutions and organising these volumes. Thank you, Valdo, your intelligent cooperation has been outstandingly useful.

Milan, February 2005 Giuseppe Allegra

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Adv Polym Sci (2005) 180: 1–16
DOI 10.1007/b107230

On the Role of the Hexagonal Phase in the Crystallization of Polyethylene

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Abstract Polyethylene forms a two-dimensional hexagonal phase, stable at $\geq\sim 3$ GPa depending on molecular length, which in recent years has been claimed to intervene in crystallization prior to the formation of the usual orthorhombic phase even at atmospheric pressure. This claim is evaluated and shown to be without substance. There is very little evidence that the theoretical possibility of thin lamellae being more stable in the hexagonal phase than the orthorhombic at atmospheric pressure, if the former has sufficiently low fold surface free energy, does occur in practice. But the existence of single crystals of the orthorhombic phase unambiguously shows that they did not have a hexagonal precursor; that would have made them threefold twins. The overwhelming mass of evidence is that orthorhombic and hexagonal phases crystallize independently in accordance with the phase diagram and kinetic competition during growth, as has been understood since the hexagonal phase was discovered.

Keywords Polyethylene · Crystallization · Hexagonal phase · Metastable phases · Size-related stability

1
Introduction

The concept of precursors to polymeric crystallization other than evolving nuclei is one that has recurred regularly since the early days of the subject so far without substantiation. As far as pre-ordering in the melt is concerned, the plausible idea that it might contain regions of aligned molecules is not supported by detailed X-ray analysis [1]. In terms of developing crystallites, three recent proposals concern origins respectively, in spinodal decomposition [2], block precursors [3] and an intermediate metastable phase, such as the hexagonal of polyethylene, in crystallization from the melt [4]. While the last of these is the particular concern of this article, fundamental difficulties in accepting the first two hypotheses may also be pointed out. First, crystallization is, in almost all circumstances, heterogeneously nucleated whereas spinodal decomposition is a homogeneous mechanism, with its own striking and characteristic morphology, e.g. [5], quite distinct from that of crystallized polymers. Second, insofar as classical thermodynamics retains its relevance to atomic dimensions, there is no obvious free energy minimum offering exceptional stability to a small block as nucleation proceeds. A particular block size is merely one stage in the progressive reduction in free energy, once the critical nucleus has been exceeded, as more stems crystallize. The addition of each stem does represent a local free energy minimum, with the positive surface contributions increasingly offset, but there is no more significant minimum which would confer exceptional stability for a particular dimension of block. Nor does a possible mesomorphic structure, of lower free energy, offer additional stability to the embryo: if it did exist it would become the preferred mode of crystallization prevailing over the observed crystal structure. *A priori*, there is no reason here to expect that crystallization proceeds other than by progressive development of the critical nucleus. Nor, as discussed below, does hexagonal polyethylene, a claimed metastable precursor to the orthorhombic phase at atmospheric pressure [4], provide an exception to this scenario. Convincing evidence in favour of precursors other than conventional nuclei playing a role in polymeric crystallization has yet to be provided.

2
Hexagonal Polyethylene

2.1
Context

The remarkable lamellar morphology of polyethylene crystallized at high pressures ∼ 0.5 GPa, with thicknesses in the micron range [6], and sometimes substantially higher [7], was eventually correlated with crystallization of a new phase of the polymer, first on thermodynamic evidence [8, 9] then confirmed by X-ray analysis [10]. The author has previously reviewed the work by which this was established and its wider context within polymeric crystallization [11]; this is still valid but is now supplemented by the important later discovery that lamellae of the hexagonal phase form circular [12]. Salient points are that two distinct crystallization processes were identified, at low and high pressures, following the recognition that the optical texture of polyethylene crystallized at high pressure differed from the spherulitic organization typical of growth at atmospheric pressure or *in vacuo* being spiky as in immature spherulites grown at low supercoolings (Fig. 1) [13, 14]. Moreover, these two different textures persisted, little changed, in products of crystallization at intermediate pressures, ∼ 0.3 GPa, when one gave way to the other over a narrow temperature interval depending on molecular length [14]. The two textures were found to form, isobarically, in different, non-overlapping, ranges of supercooling, the hexagonal first, at lower values, and to have melting points differing by ∼ 8 K according to their respective thin and thick constituent lamellae [14]. The two forms tended to occur separately, in adjacent areas, but when the orthorhombic phase did grow on an existing hexagonal lamella, it did so with sharply decreased thickness. Crucially, it was then shown that unlike crystallization at atmospheric pressure, which occurred in a single stage, that at high pressure occurred with two sequential exotherms and two associated volume changes [8, 9]. These thermodynamic data were consistent with there being two first order transitions when polyethylene crystallized at 0.5 GPa but only one at low pressures or *in vacuo*. The former circumstance corresponded, it was proposed, to sequential transformation first from the melt to a new 'intermediate' phase then from this to the orthorhombic form and a phase diagram, constructed from thermal data, published [8, 9].

In situ X-ray examination of crystallizing polyethylene, at high temperature and pressure, then confirmed this proposal in detail, showing that the wide-angle diffraction pattern changed abruptly with the optical texture [10]. That corresponding to the spherulitic texture was of the usual orthorhombic form while the new 'intermediate' phase had two-dimensional hexagonal symmetry, with an increased cross-sectional area per chain, but without

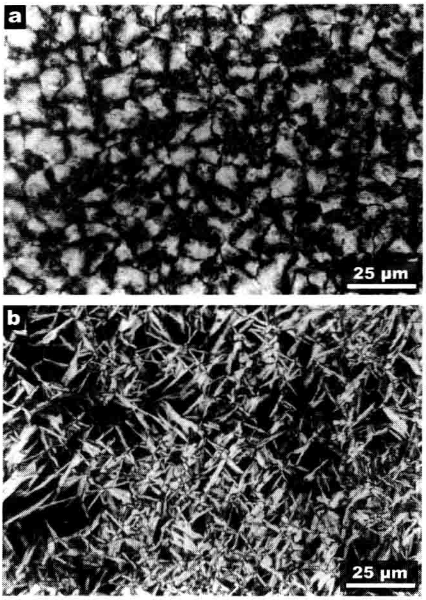

Fig. 1 The differing optical textures, between crossed polars, of linear polyethylene after crystallization from the melt at pressures close to the triple point, ~ 0.3 GPa (**a**) the conventional spherulitic texture of the orthorhombic phase (**b**) the coarse lamellar texture formed as the hexagonal phase then transformed to orthorhombic during return to ambient temperature and pressure from [14]

a single chain configuration. Models in which both TTT and TGTG* configurations exist in the same chain, where T signifies trans, G and G* alternative gauche bond sequences, are able quantitatively to account for the experimental data, such as specific volume, of the hexagonal phase [15].

The distinct nature of the high and low pressure processes was subsequently reinforced with the demonstration that they give individual lamellae of different habits (Fig. 2). Orthorhombic polyethylene crystallizes from the melt with lamellae of familiar forms [16], showing some tendency to incipient dendritic growth, elongated along *a* and *b* axes, in the changeover region, and with molecules inclined at ~ 35° to lamellae. Hexagonal polyethylene, in striking contrast, forms circular discs, thinner at their edges, to which molecules are normal [12]. These are so thick that they can be observed growing, individually, in the diamond-anvil pressure cell. The usual orientation presents lamellae in cross-section, with molecules approximately parallel to the diamond surfaces, consistent with flow during sample preparation. In this condition they display strong, clear birefringence contrast. The first observations reported that when a melt was subject to increased pressure lamellae 'flashed into view' [17] but when grown at low supercooling they can easily be held stable indefinitely. Only when the temperature is lowered sufficiently

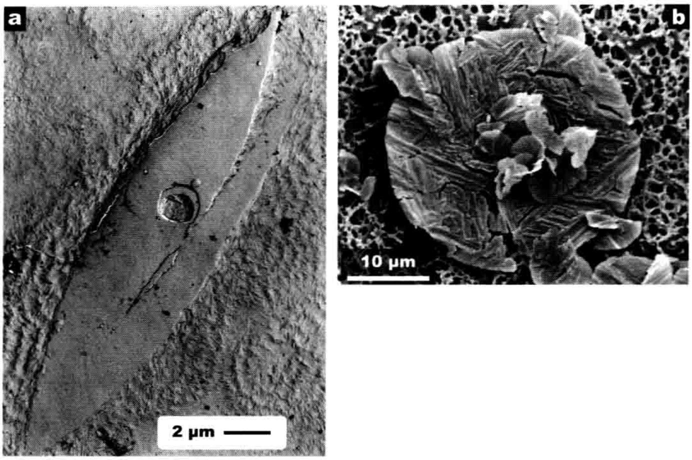

Fig. 2 Single crystals of linear polyethylene (**a**) crystallized at 130 °C at atmospheric pressure (**b**) crystallized at 0.3 GPa as uniform circular discs then given a complex twinned texture with lines inclined at ∼ 60° during return to ambient temperature and pressure from [12]

does the birefringence change and the contrast become muddy when the hexagonal phase transforms to the orthorhombic and molecules incline to lamellae [18] leaving a characteristic record in the morphology with adjacent regions having their *b* axes inclined at ∼ 60° [12]. This record is not found in lamellae of the orthorhombic form – as it would if they did have a hexagonal precursor – which are single crystalline.

2.2
The Pattern of Crystallization

The phenomena described are in detailed accord with the phase diagram [9, 11] coupled with the concept of kinetic competition during growth. The phase diagram defines those regions in which a particular phase (of infinite size) is the most stable, having the lowest free energy (specific Gibbs function). Outside its boundary lines a given phase may still exist or form but in metastable condition. There is no requirement that only the stable crystalline phase can form within its region of the phase boundary. As always in crystal growth, it is the fastest growing path which is followed as, for example, in chainfolding and the phase which appears is not necessarily the most stable. In practice, when polyethylene crystallizes at high pressures for a typical cooling rate ∼ 1 K/min it is the hexagonal phase which forms first and metastably inside the orthorhombic-stable region (Fig. 3). However, circumstances may change this outcome which is not invariably the case: the orthorhombic phase forms directly from the melt on fast quenching [19]

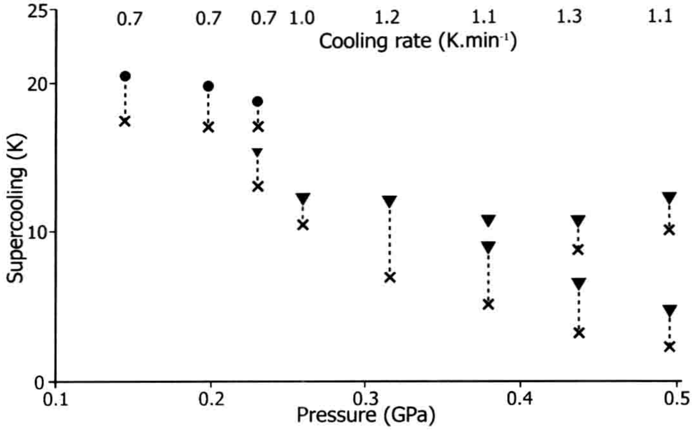

Fig. 3 A plot of the supercoolings as a function of pressure at which exotherms appear during the crystallization of linear polyethylene during cooling from the melt at the rates shown. *Crosses* show the start of the exotherms; *filled circles* show the peak temperatures for orthorhombic crystallization; *filled triangles* show the sequential peak temperatures (where resolved) corresponding first to hexagonal crystallization then its conversion to the orthorhombic phase. Redrawn from [9]

while high molecular weight polyethylene cooled at 1 K/min and 0.5 GPa, crystallizes within the hexagonal-stable region [9].

Crystallization of the metastable phase is to be expected because the typical supercooling of ~ 12 K at which the hexagonal phase then forms (Fig. 3) is greater than the width of the hexagonal-stable region at 0.5 GPa [9]. However, when forming in the orthorhombic-stable region the hexagonal phase is inevitably in kinetic competition with the formation of that phase directly from the melt. At the mutual phase line this latter is the slower process but, with increasing supercooling the free energy falls more rapidly for the orthorhombic than for the hexagonal phase so that eventually direct crystallization of the orthorhombic phase will and does prevail [19].

Similar considerations apply to crystallization at pressures below the triple point [9, 11]. Here the melting point of the hexagonal phase (for infinite thickness) is lower than the orthorhombic so that the orthorhombic phase has the higher supercooling at a given temperature, increasingly so as the pressure falls further (Fig. 4). Experimental data show that, near the triple point ~ 0.3 GPa, with a cooling rate ~ 1 K/min, the hexagonal phase crystallizes at ~ 12 K of supercooling and the orthorhombic at ~ 16 K. It is to be expected, therefore, that the hexagonal phase will continue to form first at this cooling rate and pressures reducing below the triple point until the respective supercoolings of 12 K for the hexagonal and 16 K for the orthorhombic phase occur at the same temperature. This is consistent with experiment.

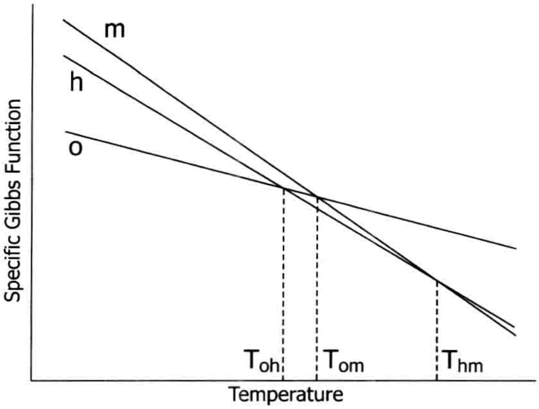

Fig. 4 Schematic free energy diagram for the crystallization of polyethylene from the melt showing the specific Gibbs function (chemical potential) for melt (m), hexagonal (h), and orthorhombic (o), phases as function of temperature

The large body of explicit evidence cited shows that the hexagonal and orthorhombic phases crystallize in two distinct, independent processes. They form with different lamellar habits and optical textures, at distinct supercoolings for the same cooling rate, with the orthorhombic phase giving substantially thinner lamellae, melting ~ 8 K lower than those formed in the hexagonal phase which, moreover, commonly forms within the orthorhombic-stable region, entirely in accord with the phase diagram. Moreover, were the orthorhombic phase to form around a hexagonal precursor, the latter would leave a characteristic twinned morphology [12]; this has never been observed.

Nevertheless, it has subsequently been suggested that, for polyethylene, there could be a phase inversion at small lamellar thickness which could make the hexagonal the precursor of orthorhombic crystallization from the melt even at atmospheric pressure [4]. The basis of this proposal will now be outlined and the conclusion reached that it is inapplicable, in part because the effective fold surface energy during growth of hexagonal lamellae is not sufficiently low.

3
Thickness-Related Stability

3.1
Thermodynamics

The relative stabilities of orthorhombic and hexagonal phases are conveniently discussed using a free energy diagram as in Fig. 4. This plots specific Gibbs functions, g, (which are equal for infinite phases in equilibrium) against temperature, T, at constant pressure, p, for the two crystalline phases and the melt. From the fundamental relation

$$\left(\partial g/\partial T\right)_p =- s\,.$$

these are straight lines of slope $-s$, the specific entropy, if variations in specific heat capacities

$$c = T\left(\partial s/\partial T\right)$$

are ignored. Moreover, to cross a boundary in a phase diagram with increasing temperature at constant pressure, and achieve the necessary decrease of free energy requires that one moves to a phase of higher specific entropy, whence

$$s_{\mathrm{m}} > s_{\mathrm{h}} > s_{\mathrm{o}} \tag{1}$$

referring to the specific entropies of melt, hexagonal and orthorhombic phases respectively and corresponding to the relative positions of the three phases in the phase diagram. This is reflected in the respective slopes of Fig. 4, in which the slope of the hexagonal line must lie between those of orthorhombic and melt.

Figure 4 shows relative free energies when the hexagonal phase is stable. This occurs when the orthorhombic and hexagonal lines intersect, at T_{oh}, below the orthorhombic melting temperature, T_{om}, followed by the melting of the hexagonal phase at T_{hm}. The interval $(T_{\mathrm{hm}} - T_{\mathrm{om}})$ is a measure of the relative stability of the hexagonal phase reflecting, as Fig. 4 shows, the difference in specific free energy of the two phases at T_{om}, and vanishing at the triple point, T_{t}, when all three lines have a common intersection. For lower temperatures, $T < T_{\mathrm{t}}$, as mentioned above $T_{\mathrm{hm}} < T_{\mathrm{om}}$ and the hexagonal phase is metastable by an amount proportional to $(T_{\mathrm{om}} - T_{\mathrm{hm}})$.

3.2
Stability Inversion with Lamellar Thickness

The lamellar habit adopted by crystalline polymers adds surface terms to the specific Gibbs function (chemical potential), most importantly the fold surface free energy, σ_{e}, which contributes $2\sigma_{\mathrm{e}}/\lambda\varrho$ for a lamella of thickness λ and crystalline density ϱ. In consequence melting points are lowered from T_{m}^0, for infinite thickness, to T_{m} according to the Hoffman-Weeks equation

$$T_{\mathrm{m}} = T_{\mathrm{m}}^0(1 - 2\sigma_{\mathrm{e}}/\lambda \cdot \Delta h_{\mathrm{v}}) \tag{2}$$

where $\Delta h_{\mathrm{v}} = \Delta h \cdot \varrho$ is the specific enthalpy of melting per unit volume of crystal (as opposed to Δh, the specific enthalpy per unit mass).

As a straightforward consequence, one may shift the lines in Fig. 4 upwards by $2\sigma_{\mathrm{e}}/\lambda\varrho$ for each crystalline phase to obtain a modified diagram pertinent