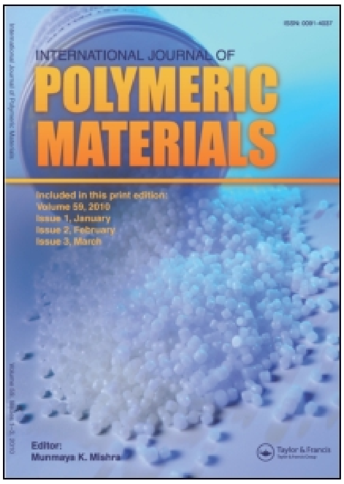

International Journal of Polymeric Materials
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713647664

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To cite this Article Pereira, Romeu A. , Dias, Marcos L. and Mano, Eloisa B.(2000) 'Orthorhombic-hexagonal Phase Transition in High Density Polyethylene Crystals', International Journal of Polymeric Materials, 45: 1, 69 — 78

To link to this Article: DOI: 10.1080/00914030008034871

URL: http://dx.doi.org/10.1080/00914030008034871

Intern. J. Polymeric Mater., 2000, Vol. 45, pp. 69-78
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Orthorhombic-hexagonal Phase Transition in High Density Polyethylene Crystals

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(Received 29 June 1998)

The crystal structure of drawn samples of high density polyethylene was investigated by using wide-angle X-ray scattering (WAXS) with CoKα and MoKα radiations. HDPE films with fiber-like morphology and constrained to a constant length on heating were studied in the range from room temperature to 158°C. Orthorhombic-hexagonal phase transition, which was previously reported only for UHMWPE fibers, was also proved to exist in moderate molecular weight HDPE drawn films. Differently from the orthorhombic phase, which melts at 129°C, the hexagonal phase formed melts at 158°C. A new hexagonal reflection with interplanar distance 2.139(7) Å, indexed as (101), is reported.

Keywords: Polyethylene drawn films; phase transitions; fiber period in hexagonal crystal; chain orientation

INTRODUCTION

Polyethylenes are semi-crystalline polymers in which crystals are constituted of folded or extended chain lamellar structures with zig-zag polymethylene chains placed like parallel sticks organized in an orthorhombic lattice. Although the presence of the hexagonal phase, also called rotator phase, is sometime reported for linear polyethylene

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chains [1], its formation from orthorhombic crystals only occurs under special circumstances.

The earliest recognized example of orthorhombic-hexagonal phase transition was reported in low molecular weight polyethylenes, specifically C23–C40 *n*-paraffins [2]. It is a first order transition which is observed a few degrees below the melting point when the sample is heated; this temperature increases with increasing chain length [3–5].

In higher paraffins and very high MW polyethylenes the orthorhombic-hexagonal transition is not shown on heating because it occurs at temperatures above the T_m. Usually the conditions for observation are those to produce an increase of T_m so that melting takes place above that transition temperature [6].

For instance, moderate and ultra high molecular weight polyethylenes show hexagonal phases under application of high hydrostatic pressure at adequate temperatures [7–10]. Orthorhombic-hexagonal transformation on heating irradiated moderate MW samples was reported [6]. The hexagonal phase was also found in some ethylene–propylene–diene terpolymers at room temperature [6]. Ultra high MW highly extended fibers constrained to a constant length can also developed hexagonal phase on heating [11–15].

In the present communication we report the orthorhombic-hexagonal phase transition observed on heating moderate molecular weight HDPE drawn films constrained to a constant length.

EXPERIMENTAL

Sample

High density polyethylene was taken from a commercial sample BT003 (Polialden), $M_w = 84800$, $M_w/M_n = 13$, $MFI = 0.3\,\mathrm{g/10\,min}$, density $= 0.95\,\mathrm{g/cm^3}$, $T_m = 129°\mathrm{C}$.

Hot-drawn sample for WAXS measurements was obtained from HDPE films prepared by compression molding at 188°C for 5 minutes and quenched at 0°C. From this film 50 × 10 × 2 mm HDPE strips were cut and submitted to a thermal treatment at 110°C for 36 hours, then cooled to 23°C and re-heated again at 5°C/min to 100°C, being immediately drawn 9 times their sizes at 100°C. The films was 0.71 mm thick with fibrillar features characterized by a rainbow texture from polarized light, indicative of high degree of orientation. From the central part of the drawn pieces, a 15 × 2 mm rectangular sample was cut and firmly held at the sample holder in the temperature chamber probe, in order to hinder free contraction upon heating.

WAXS Measurements

A standard Seifert-FPM GmbH diffractometer equipped with a graphite monochromator in the scattered beam, operating with CoKα or MoKα radiation (λ = 1.7902 Å and 0.7107 Å, respectively) in 40 kV and 30 mA was used. WAXS measurements were carried out in a step-by-step mode, $\theta-2\theta$ Bragg–Brentano focusing condition, with 0.25° divergent slit in the primary beam and 0.05° in the scattered beam. The interval from 5 to 90° in 2θ was investigated.

WAXS photographs were recorded with the incident beam perpendicular to the specimen surface in a Läue chamber. The exposure time was around 2 hours. WAXS photographs at different desired temperatures were obtained using a chamber previously reported [16], specially designed for this work. The chamber was coupled to the goniometer axis so that the conditions could be established at a chosen temperature from −160 to 180°C.

Crystal lattice parameters were obtained refining the WAXS patterns by using the Rietveld Analysis Program DBWS-9411, and atomic position parameters from Kavesh and Schultz model of polyethylene unit cell [17].

RESULTS AND DISCUSSION

In polyethylene orthorhombic crystals, chains are parallel to the *c* axis of the unit cell; the central chain in *ab* plane is not crystallographically equivalent to the chains located at unit cell corners [18].

The *a* and *b* axis in the orthorhombic-hexagonal transition are related by $a/b = \sqrt{3}$, and all chains in the crystal must have crystallographic equivalence. This means that the setting angle, ψ approaches 90°, and the symmetry order becomes 3 or 6.

Figure 1 shows a sequence of WAXS photographs of HDPE maintained at constant length and heated from room temperature to 155°C. No structural change was observed up to 145°C. From this temperature on, the reflections became arched, indicating loss of molecular orientation in relation to the draw direction. The equatorial reflections (020) and (310) are split, and at 148°C (Fig. 1C) two new reflections appear. In addition to the two new reflections developed from 148°C, the photography obtained at 155°C from a sample placed with a 15° angle between the draw direction and the X-ray incident beam (Fig. 1E), shows the presence of another reflection with a marked azimuthal and radial broadening as indicated by the arrow (4). Arrows (1) and (2) are the new equatorial reflections, and the (3) one appear in radial positions as that of the $(201)_{ort}$ reflection with higher azimuthal angle.

The arrow (5) discloses the reflection $(002)_{ort}$, which is arched, broader and less intense than that showed by arrow (4), suggesting loss

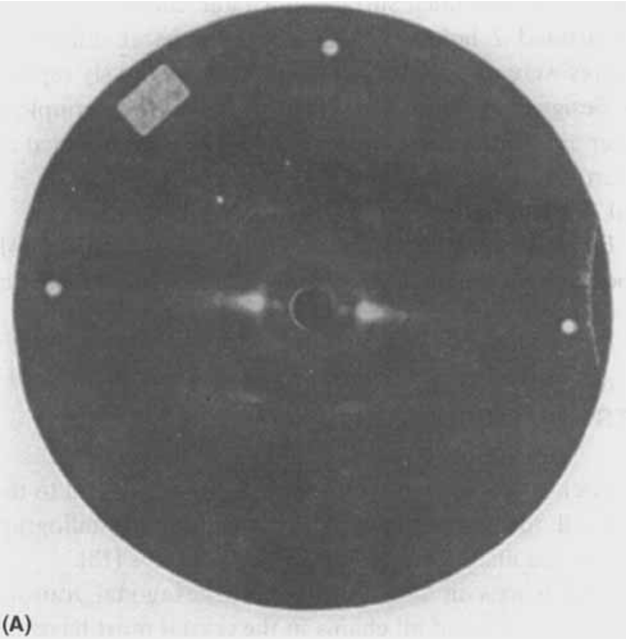

FIGURE 1 WAXS photographs of drawn HDPE maintained at constant length at (A) 23°C, (B) 145°C, (C) 148°C, (D) 151°C, (E) 155°C; MoKα radiation.

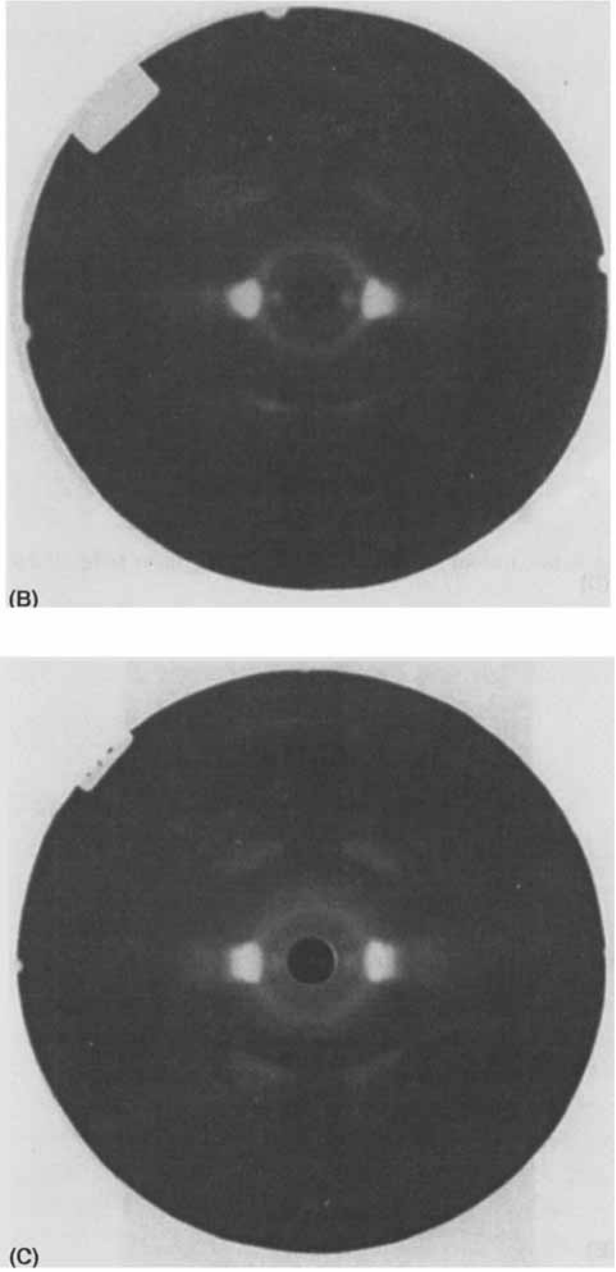

FIGURE 1 (Continued).

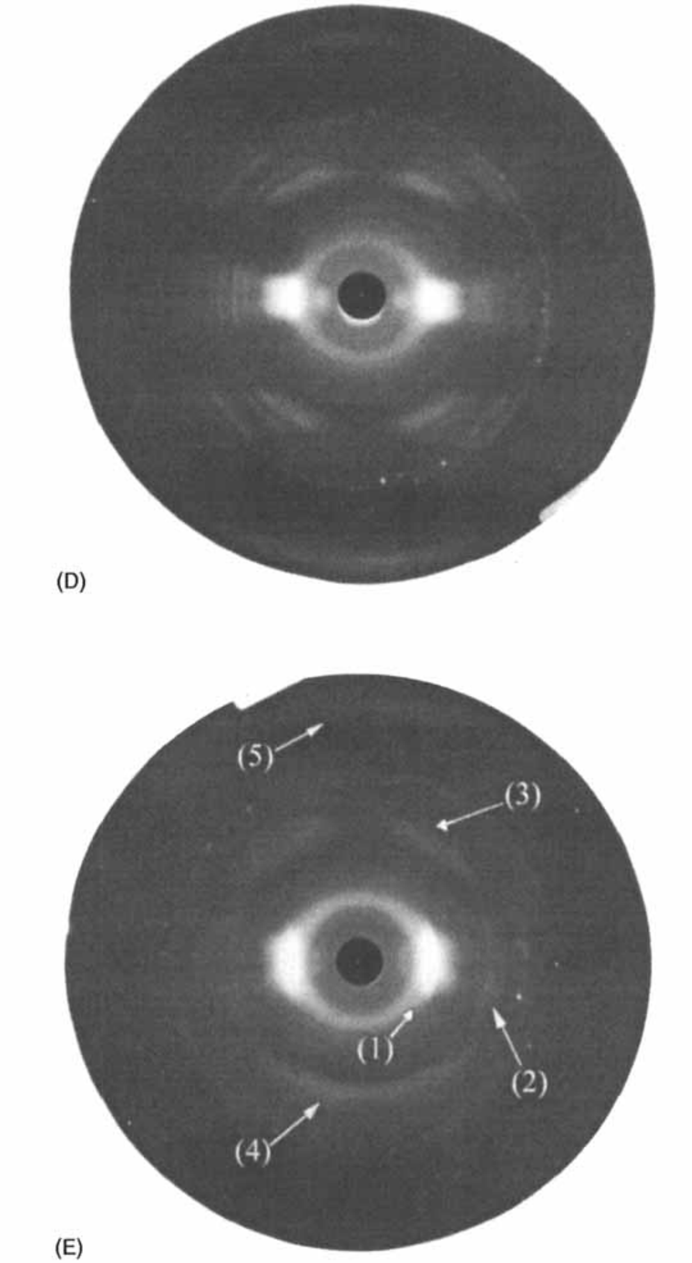

FIGURE 1 (Continued).

of orientation and increasing of molecular longitudinal chain disorder. The increasing of intensity of the reflection indicated by arrow (4) evidences the hexagonal crystals predomination from this temperature. The orthorhombic lattice reflections located at equator have weak intensities, except in planes (110) and (200), which are split showing the presence of two orthorhombic crystalline lattices. DSC analysis confirming the presence of this two types of crystals were previously reported [16].

Photographs obtained at Läue chamber give important information on possible changes that take place in the sample structure on heating. Nevertheless, accurate data on lattice parameters and reflection intensities require step-by-step azimuthal scans in 2θ obtained in the diffractometer. WAXS curves in the azimuthal section $\Psi = 90°$ at a temperature range in which the orthorhombic phase and the new phase developed from 148°C are coexistent, are shown in Figure 2. At

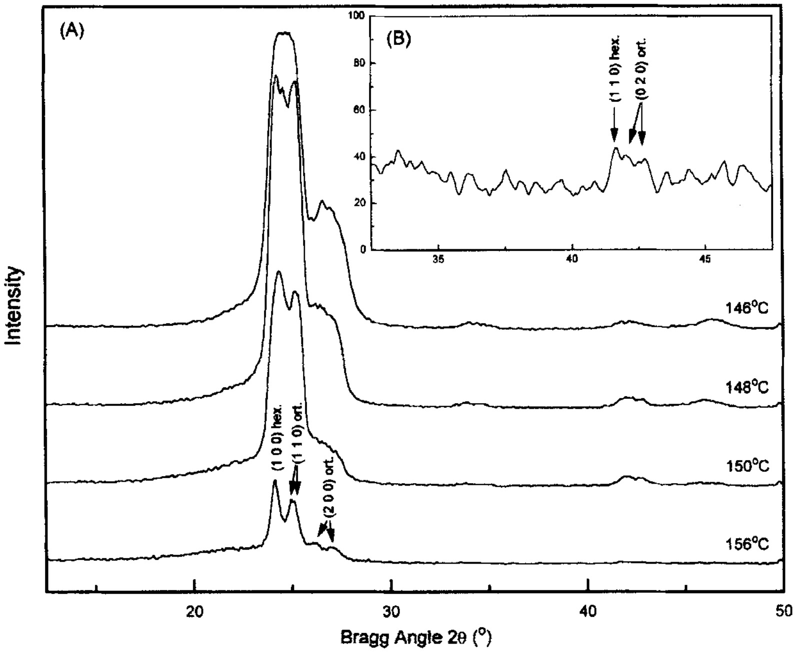

FIGURE 2 HDPE WAXS patterns of equatorial reflections at different temperatures; CoKα radiation. (A) Whole pattern; (B) Details of 30–50° 2θ range at 156°C.

156°C, the reflections $(110)_{ort}$, $(200)_{ort}$ and $(020)_{ort}$, the last one showed in Figure 2B, are split. The hexagonal phase reflection, indicated by arrows (1) and (2) in Figure 1E became visible.

Indexing the hexagonal reflections with Miller notation (100) and (110), the ratio between interplanar spacing is equal to 1.73, which corresponds to planes of a Bravais hexagonal lattice. Azimuthal sections at $\Psi = 0°$ and sample axis 15° inclined in relation to the incident beam are disclosed in Figure 3. At 151°C, the amorphous halo, a broad and diffuse reflection (arrow 4), a reflection indexed as $(101)_{hex}$ (arrow 3) and the $(002)_{ort}$ one are present. Increasing temperature initially provokes an increase in the reflection indicated by arrow 4 which disappears at 158°C when the melting of the sample occurs. In Table I is shown the crystallographic data obtained by adjusting the reflection by a symmetrical function composed of Gaussian and Cauchy profiles and carrying out refinement of indexed patterns .

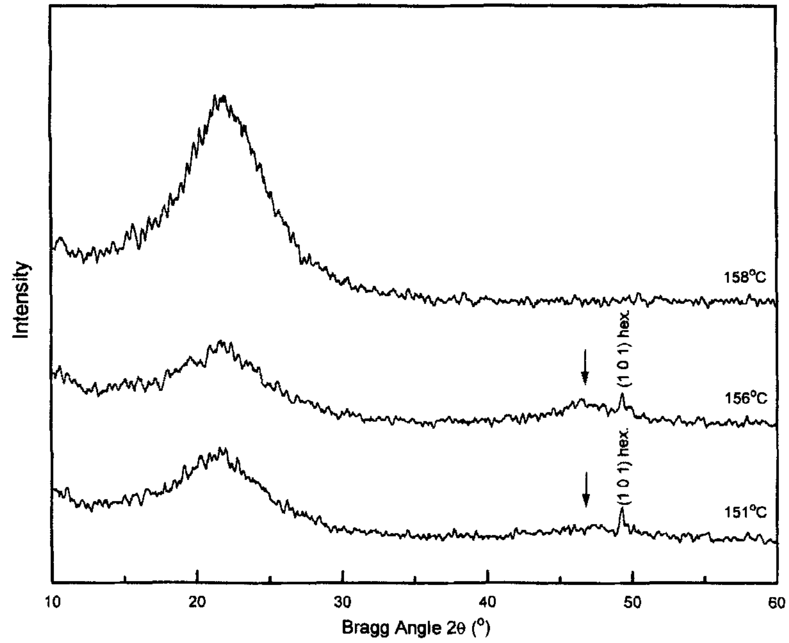

FIGURE 3 HDPE WAXS patterns of meridional reflections at different temperatures; CoKα radiation.

TABLE I Crystallographic data of hexagonal crystals in moderate MW drawn HDPE films

$T(°C)$	$d_{[100]}(Å)$	$d_{[110]}(Å)$	$d_{[101]}(Å)$	$d_{[100]}/d_{[110]}$	$a(Å)$	$c(Å)$
148	4.242(5)	2.451(6)	2.139(7)	1.731	4.9114(15)	2.476(7)
152	4.263(5)	2.460(8)	2.132(4)	1.732	4.927(9)	2.461(6)
156	4.286(6)	2.473(7)	2.124(5)	1.733	4.948(6)	2.446(5)

Reflection 4, in radial position of the first layer is $0.42\,Å^{-1}$ from equator; it corresponds to a value of 2.38 Å and is related to the fiber period in the crystal [8]. This value do not correspond to $c = 2.476(7)$ Å as determined by refinement and can be attributed to the presence of paracrystalline disorder, according to Lindenmeyer and Hosemann [19]. The meridional reflections ($\psi = 0°$) are broader and more arched as the temperature is raised, indicating loss of chain orientation in relation to the draw direction.

If no contraction during heating of the fibers is allowed, the polymer chains is maintained stretched and configurational melt entropy $\Delta S_{\text{ort}\rightarrow\text{liq}}$ decreases, increasing T_m to a value above the orthorhombic-hexagonal phase transition [6]. This transition, reported previously only for UHMWPE fibers in the condition similar to that used in this work, seems not to be dependent on molecular weight at least in the range used in commercial applications as shown by our results.

Acknowledgments

The authors are indebted to Miss Aline Moojen Pedreira for her efficient help in the preparation of this manuscript. This work was supported by the Brazilian agencies *Conselho Nacional de Desenvolvimento Científico e Tecnológico* (*CNPq*) and *Coordenação do Aperfeiçoamento de Pesquisa de Nível Superior* (*CAPES*).

References

[1] Müller, A. (1930). *Proc. Roy. Soc.*, **A127**, 417–32.
[2] Müller, A. (1927). *Proc. Roy. Soc.*, **A114**, 5427–60.
[3] Schaerer, A. A., Busso, C. J., Smith, A. E. and Skinner, L. B. (1955). *J. Am. Chem. Soc.*, **77**, 2017–19.
[4] Doucet, J., Denicolo, I., Craievich, A. and Collet, A. (1981). *J. Chem. Phys.*, **75**(10), 5125–5127.

[5] Doucet, J., Denicolo, I. and Craievich, A. (1981). *J. Chem. Phys.*, **75**(3), 1523–1529.

[6] Ungar, G. and Keller, A. (1980). *Polymer*, **21**, 1273.

[7] Bassett, D. C., Block, S. and Piermarini, G. J. (1974). *J. Appl. Phys.*, **45**, 4146.

[8] Yamamoto, T., Miyaji, H. and Asai, K. (1977). *Jap. J. Appl. Phys.*, **16**(11), 1891–1898.

[9] Tsubakihara, S., Nakamura, A. and Yasuniwa, M. (1991). *Polym. J.*, **23**(11), 1317–1324.

[10] Yasuniwa, M., Enoshita, R. and Takemura, T. (1976). *Jap. J. Appl. Phys.*, **15**(8), 1421–1428.

[11] Pennings, A. J. and Zwijnenburg, A. (1979). *J. Polym. Sci., Phys. Ed.*, **17**, 1011–1032.

[12] van der Werff, H. and Pennings, A. J. (1991). *Colloid Polym. Sci.*, **269**, 747–763.

[13] Antipov, E. M., Kulichikhin, V. G. and Plate, N. A. (1992). *Polym. Eng. Sci.*, **32**(17), 1188–1203.

[14] Wasiak, A. and Sajkiewicz, P. (1993). *J. Materials Sci.*, **28**, 6409–6417.

[15] Uehara, H., Kanamoto, T., Kawaguchi, A. and Murakami, S. (1996). *Macromolecules*, **29**, 1540.

[16] Pereira, R. A., Mano, E. B. and Dias, M. L. (1997). *Polymer Testing*, **16**, 589–601.

[17] Kavesh, S. and Schultz, J. M. (1970). *J. Appl. Polym. Sci.*, A-2, **8**, 243.

[18] Bunn, C. W. (1939). *Trans. Faraday Soc.*, **35**, 482.

[19] Lindenmeyer, P. H. and Hosemann, R. (1963). *J. Appl. Phys.*, **34**, 42.