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The influence of side branches on the structure of crystalline phase in ethylene-1-alkene copolymers

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Abstract

The influence of side branches on the unit cell dimensions in ethylene-1-alkene copolymers was investigated both at room temperature as well as during heating of the samples up to melting. Time resolved X-ray diffraction investigations revealed that in the case of ethylene-1-octene copolymers with low and moderate comonomer content, the transversal expansion of the unit cell occurs due to the limited thickness of lamellae, however the samples with higher comonomer content (above 5 mol%) exhibit distinctly larger expansion resulting from the stresses imparted on the basal surfaces of crystals by the excluded branches. At high temperatures, independently on the thermal expansion, an additional increase of the unit cell volume occurs, caused probably by a penetration of the end-parts of side branches, residing near the crystals surface, into the surface cells. Similar phenomenon is observed for ethylene-1-butene copolymer. On contrary, the ratio of the average unit cell volume in ethylene-1-propene copolymer to the unit cell volume in linear polyethylene at the same temperature, decreases starting from about 50 °C. Such a behavior is a new confirmation of a partial inclusion of methyl branches into the crystalline phase. Most probably, when the temperature increases, the volume of included branch becomes a decreasing fraction of the thermally expanding unit cell volume.

Keywords: Ethylene-1-alkene copolymers; Crystalline phase; Unit cell

1. Introduction

The presence of local structural constraints in the molecular chains of polymer during its solidification affects considerably the process of primary crystallization, controls its extent and influences the crystallizability of the amorphous phase remaining after the first stages of crystallization. Such specific constraints exist in the copolymers composed of crystallizable and noncrystallizable comonomers, as an example of which may serve homogeneous ethylene-1-alkene copolymers. The 1-alkene comonomers introduced into the structure of polyethylene macromolecule, form short side branches which disrupt the regularity of the main chain and generate a distribution of ethylene sequences of different lengths. When the number of branches increases, one observe a decrease in the degree of crystallinity, lateral sizes of crystallites and the thickness of crystalline lamellae [1–4]. The presence of side branches influences also the internal structure of crystalline phase. Two different theories related to this effect have been elaborated. Thermodynamic considerations based on equilibrium

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conditions predict that only the ethylene sequences are involved in crystallization [5–7]. The branches are therefore completely rejected from the crystallites and the degree of crystallinity is controlled by the ethylene sequences length distribution. Kinetic theories, pointing that equilibrium state is not achieved during polymer crystallization and defects are partitioned between amorphous and crystalline regions, permit partial incorporation of the side branches into the crystallites as lattice defects [8]. Experimental data on the branches location, result mostly from X-ray diffraction [9–17] and solid state ^{13}C NMR studies [18–21]. The first method is used for the determination of the unit cell parameters. The second one investigates the chemical shift of carbon atoms in the branches as a function of the environment in which they are located.

X-ray diffraction data show that the *c*-edge of the orthorhombic unit cell, parallel to the chains axis, practically does not depend on the branch content [10,14,16] and is equal to that one of linear polyethylene. On contrary, the edges *a* and *b*, perpendicular to the chain axis, progressively increase with increasing comonomer concentration. Methyl branches produce more pronounced increase than the longer ones all of which have similar effect [14,16]. This expansion is explained as caused by the inclusion of side branches into the crystalline phase. It is widely acknowledged, that the degree of incorporation depends on the branch size, reaching the highest level for methyl branches. As concerns the longer ones, different opinions are presented. Some authors stated that only methyl branches can be incorporated [11,12]. Others [14], reported a very limited inclusion of ethyl ones. Vonk proposed that even longer branches can be incorporated by substitutional solution [13].

However, it was also observed that the unit cell parameters of completely linear polyethylene depend on the crystallization conditions and increase clearly when the thickness of crystalline lamellae decreases [22,23]. Such a behavior was attributed to the changes in the interactions between the neighboring chains near the crystal surface and surface stresses imposed by chain folding. Earlier, such an effect was observed for *n*-paraffin crystals [24] and confirmed by theoretical normal mode calculations [25] which revealed a big influence of the length of *n*-paraffins chains on the specific volume of crystalline phase, showing that the volume increases with decreasing chain length. For this reason, another interpretation, proposed already by Bunn [26] was formulated [14]. According to it, the unit cell expansion in copolymers results mostly from the reduction of crystal thickness caused by the presence of side branches which cannot be included into the crystal lattice.

On the other hand, ^{13}C NMR investigations indicate that quite a high fraction of branches, at least of the shorter ones, is incorporated into the crystalline phase. For methyl branches, the reported fraction varies from 22% [18] and 25% [19] up to 50% [20]. However, the last value has been determined for a copolymer containing 20 mol% of propene in which only hexagonal crystalline phase exists. In the case of ethyl and hexyl branches, the fractions of 10% and 6% respectively are reported [21,18].

Summarizing, the average volume of a copolymer unit cell can increase as a result of two different deformation mechanisms: inclusion of the branches, which is much more frequent for the shorter ones, and crystal thickness reduction, caused by the longer side branches which are excluded from the crystals.

In this work, the effect of side branches on the structure of crystalline phase of a set of ethylene-1-alkene copolymers was investigated by means of X-ray diffraction method. The measurements were performed not only at room temperature but also during heating of the samples up to complete melting. The measurements were undertaken in order to investigate in which way the two sources of the unit cell expansion i.e. inclusion of the short side branches and limitation of crystal thickness due to the long branches exclusion, act at high temperatures, when additionally thermal expansion occurs and changes the interaction between the molecular chains. The behavior at high temperatures has been compared with the results obtained at room temperature. The investigations were performed for the copolymers of ethylene with 1-propene, 1-butene and 1-octene. Linear polyethylene was also investigated as a reference material. Parameters of the unit cell were calculated from WAXS patterns. SAXS method was used for the determination of the thickness of crystalline lamellae.

2. Experimental

2.1. Material

The homogeneous copolymers of ethylene and 1-alkenes used in the present work were synthesized at DSM Research using a metallocene catalyst system. The density, mole % of comonomer, melt flow index (I_2) and molecular mass provided by the producer are given in Table 1. The short-chain branch number per 1000 carbon atoms (SCB/1000C) was calculated from the number of CH_3 groups per 1000 carbon atoms given by the producer. Sample code for ethylene-1-octene copolymers indicates the rounded mole % of comonomer. The linear polyethylene LPE (DSM code JW1114), which was investigated in this work as the reference sample, was synthesized using a vanadium based catalyst. It has a weight-average molar mass M_w of 52.3 kg/mol and a polydispersity M_w/M_n of 3.2.

Most of copolymers have similar molecular weight ($I_2 \approx 1$–2.4) except for one with lower molecular weight sample EO7 ($I_2 = 25.77$).

Table 1
Copolymer characteristics

Sample code	Branch type	Density (23 °C) [kg/m^3]	SCB/ 1000C	Mole % of comonomer	I_2 [dg/min]	M_n [kg/mol]	M_w [kg/mol]
EO1	Hexyl	948.1	4	0.8	2.39	–	–
EO2	Hexyl	928.7	8.9	1.77	1.64	–	–
EO4	Hexyl	907.7	21.7	4.34	1.38	–	–
EO6	Hexyl	899.9	27.5	5.5	1.04	36	88
EO7	Hexyl	899.3	33.2	6.6	25.77	–	–
EO9	Hexyl	880.1	45.3	9.15	1.23	39	87
EP	Methyl	912.1	26.9	5.38	2.15	28	68
EB	Ethyl	888.6	43.0	8.6	1.74	36	86

2.2. Methods

X-ray diffraction patterns of the samples were registered both at 20 °C as well as during heating at the rate of 10 °C/min, from 20 °C up to complete melting. Before the measurements, all the samples were melted at 180 °C (or at 160 °C in the case of EO7, EO9 and EB samples) to erase their thermal history and cooled at the same rate of 10 °C/min to 20 °C. Melting temperatures were established from previous DSC measurements. Time resolved wide angle (WAXS) and small angle (SAXS) X-ray diffraction investigations were performed using the X33 double focusing camera [27] of the EMBL (HASYLAB), on the storage ring DORIS of the Deutsches Elektronen Synchrotron (DESY). The patterns were recorded using a standard data acquisition system with two linear delay line detectors connected in series [28,29]. The wavelength of X-rays was 1.5 Å. The samples with a thickness of 1 mm were sealed between thin aluminum foils. The temperature of the sample was controlled by a Mettler FP-82HT hot stage. During heating, diffraction patterns were registered every 6 s giving the resolution of 1 °C for each pattern. Data processing was preceded by their normalization to the intensity of primary beam and correction for the detector response. Three strong and sharp reflections 0 1 0, 1 1 0 and 1 0 0 of the β-form of tripalmitin [30] were used for calibration of 2θ axis in the case of WAXS detector. The registration range was: $8.35° < 2\theta < 38°$. SAXS detector was calibrated using first nine orders in the scattering pattern of dry calcified collagen with the spacing of 640 Å. SAXS patterns were registered in the range of $2.23 \times 10^{-3}\,\text{Å}^{-1} < s < 4.45 \times 10^{-2}\,\text{Å}^{-1}$ where $s = 2\sin\theta/\lambda$, 2θ is the scattering angle and λ is the wavelength of the radiation. They were corrected for the scattering coming from the sample holder, and residual inhomogeneities inside the samples by subtracting from each particular scattering curve of a sample, the averaged pattern of the same sample in the molten state [31].

DSC measurements were performed using a Perkin–Elmer Pyris 1 apparatus. The temperature of a sample was calibrated using the melting point of benzophenone (48 °C) and indium (156.6 °C). The heat flow rate was calibrated with the specific heat of fusion of indium (28.45 J/kg). The block containing the measuring unit was thermostated at −10 °C with liquid nitrogen and the measuring cell was flushed with nitrogen gas. The same thermal program as in X-ray diffraction experiments was employed: the sample was initially melted at 180 °C and after 5 min cooled at 10 °C/min to 20 °C. In the next step, after about 5 min residence time, the sample was heated at the same rate to 180 °C.

DSC thermograms registered during heating, normalized with sample mass and heating rate, were used in calculations of the mass fraction crystallinity employing the method of Mathot and Pijpers [32].

2.3. Data elaboration

Lorentz corrected WAXS curves were analyzed using a computer program *OptiFit* [33]. In this program, experimental curve $I_E(x)$ is approximated by a theoretical curve $I_T(x)$ which is a sum of functions describing crystalline peaks 110 and 200, amorphous halo and the background. Both crystalline peaks and amorphous halo are represented by functions $F_i(x)$ which are linear combinations of Gauss and Lorentz functions:

$$F_i(x) = f_i H_i \exp\left\{-\ln 2\left[\frac{2(x - x_{oi})}{w_i}\right]^2\right\} + \frac{(1 - f_i)H_i}{1 + [2(x - x_{oi})/w_i]^2} \qquad (1)$$

where x is the scattering angle 2θ, H_i, w_i and x_{oi} are respectively the peak height, width at the half height and the center. The shape coefficient f_i is equal to 1 for the Gauss profile and 0 for the Lorentz one. The background is described by a third order polynomial. The function $I_T(x)$ is fitted to the experimental intensity profile $I_E(x)$ by minimization of the sum of squared deviations using optimization procedure of Powell [34].

Based on the as determined positions of 1 1 0 and 2 0 0 peaks, the lengths of the edges a and b of the orthorhombic unit cell, perpendicular to the chain axis were calculated. Volume of the unit cell was calculated assuming a constant value of the c-edge [10,14,16] and equal to that one of linear polyethylene $c = 2.547\,\mathring{A}$ [10].

SAXS patterns, after the initial normalization and corrections described above, were interpreted as the scattering intensity distributions originating from the stacks of lamellae and arising from the periodic fluctuations of the electron density in the alternating amorphous and crystalline regions. The morphological parameters of such lamellar systems were determined calculating the linear correlation function $K(x)$, employing the method elaborated by Strobl and Schneider [35] and the computer program OTOKO [36]. As this method cannot be used when the volume fraction crystallinity lies in the range $0.4 < X_V < 0.6$ [37], the thickness of lamellae for the samples EO2 and EP at room temperature was calculated using the long period determined from the correlation function and the mass fraction crystallinity determined by DSC method [32]. The DSC mass fraction crystallinity was firstly transformed into the volume crystallinity using the densities of amorphous and crystalline phases given by Swan [38] and next multiplied by the long period giving the thickness of lamellae.

3. Results and discussion

At room temperature, the unit cell parameters a and b increase nearly linearly with the number of short branches. Fig. 1 presents their dependence on the short branch content. The average values from the temperature range 21–25 °C are given. For 1-octene copolymers the increase in the range 0–45 SCB/1000C, amounts to about 2% and 1.5% for a and b respectively. In the case of EP copolymer, the b-edge length is close to that one of EO copolymer with similar branch content, but the a-edge is much longer. It means that the shape of the unit cell of EP copolymer is considerably changed, as compared with that one of EO copolymer and LPE. This fact is clearly visible in Fig. 2, where the ratio $k = a/b$, called later as a shape factor, is plotted versus SCB/1000C. One can also see, that for low branch content, up to about 25 SCB/1000C, the shape factor of the unit cell of EO copolymers is the same as that one of LPE. However for higher comonomer concentration, the unit cell changes in a similar way as in the case of EP sample i.e. the shape factor increases. EB copolymer shows an intermediate degree of the unit cell shape transformation.

The increase of the unit cell dimensions in the direction perpendicular to the molecular chains is accompanied with a fast decrease of the lamellar thickness, as can be seen in Fig. 3. It is important to notice, that the thickness of lamellae in EP is clearly higher than in EO copolymer with the same short branch content. Similar relation holds in the case of the crystallinity (Fig. 4).

The relation between the unit cell dimensions and the crystal thickness can be analyzed by means of a graph used by Davis and co-workers [22,23] for n-paraffins and for lamellar crystals in linear polyethylene. In this graph, the effective chain cross section (ECCS) = $ab/2$ is plotted versus the reciprocal of the lamella thickness C. A plot of this type is shown in Fig. 5, where apart from the experimental data obtained in this work (points), two straight lines are also shown. The line (a)

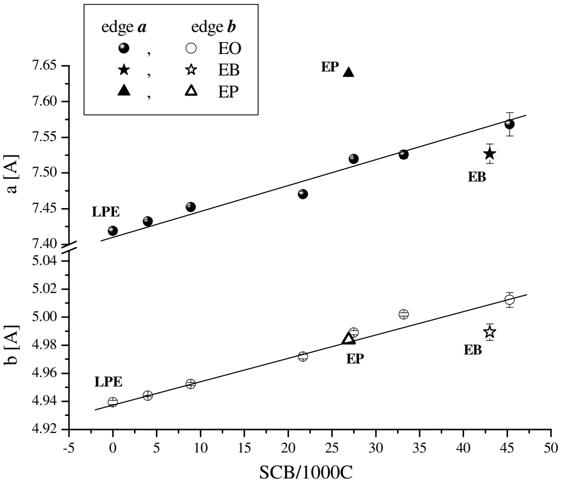

Fig. 1. The length of a- and b-edges of the orthorhombic unit cell versus the short branch content. (SCB/1000C—number of side branches per 1000 carbon atoms in the main chain). Presented values were averaged over 5 data points from the temperature range 21–25 °C. Error bars represent the standard deviations. The error bars are not used when standard deviation is smaller than the size of symbols.

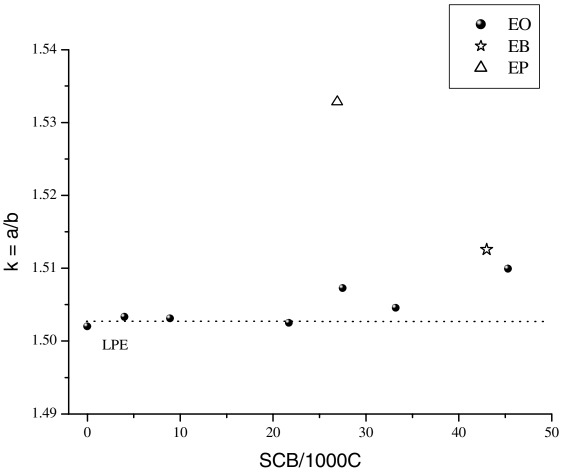

Fig. 2. Shape factor $k = a/b$ of the unit cell as a function of branch concentration.

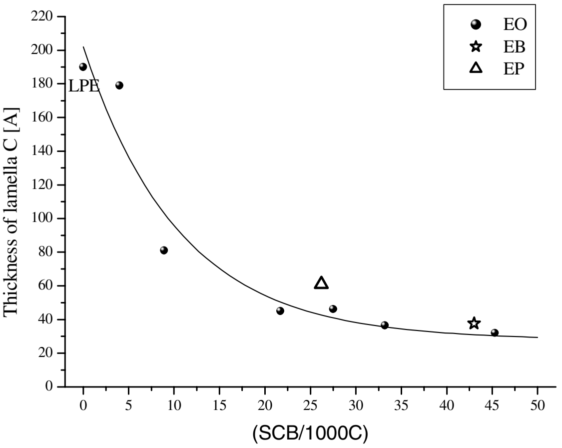

Fig. 3. Thickness of the crystalline lamellae as a function of branch concentration.

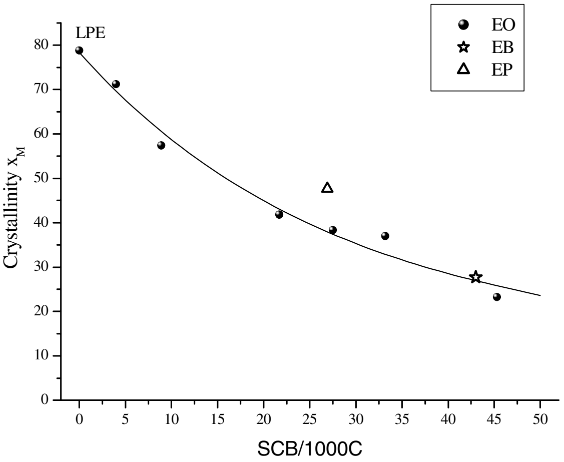

Fig. 4. Degree of crystallinity determined with DSC method as a function of branch concentration.

which is solid in the first part and dotted in the other part, has been drawn according to the formula found by Davis et al. [23] for LPE:

$$\frac{ab}{2} = 18.235 + 0.16 \cdot \frac{100}{C} \tag{2}$$

The solid part of this line is related to the range of 100/*C* values for which the dependence (2) has been experimentally established [23], while the dotted part is an extrapolation to higher values. As it results from Eq. (2), the ECCS in LPE increases linearly with the reciprocal of the lamella thickness. Based on this result, Davis and co-workers have concluded [22,23], that the increase in LPE unit cell dimensions is caused by a limited thickness of lamellae and surface stresses imposed by chain folding.

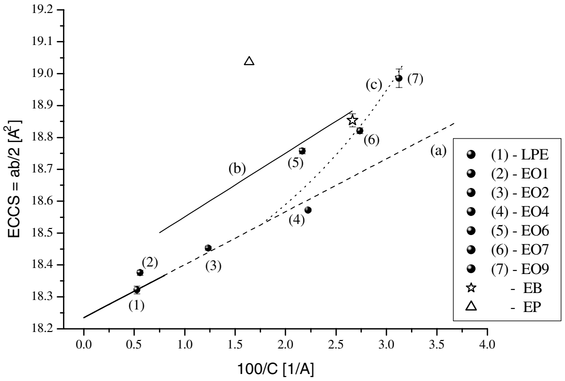

Fig. 5. Effective chain cross section (ECCS) = *ab*/2 versus the reciprocal of the lamella thickness 100/*C*. Solid part of the straight line (a) represents the data of Davis et al. [23] and the dotted part of this line is an extrapolation to higher values. Line (b) represents the data of Howard and Crist [14]. Line (c) is described in the text.

The second straight line (b) represents the data obtained by Howard and Crist [14] for ethylene-1-butene copolymers. The two lines (a) and (b) have a similar slope but clearly differ in the intercept indicating, that even for relatively thick crystals, the unit cell of ethylene-1-butene copolymers is distinctly bigger than that one of LPE, which in turn means, that not only limited crystal thickness is responsible for the unit cell expansion in these copolymers. This has been interpreted [14] as a result of partial incorporation of ethyl branches into lamellar crystals. As one can see, the ECCS of EB copolymer investigated in the present work fits quite well to this line.

Fig. 5 shows, that for EO copolymers with thicker lamellae (up to $100/C \leqslant 2.2$), the ECCS values fit very well to the line (a) obtained for a completely linear polyethylene, confirming that no inclusion of hexyl branches take place and the reasons of the unit cell expansion are the same as in LPE. Comparing with Fig. 3 one can see, that the number of side branches for these copolymers is below 25/1000C. However, for higher branch content and consequently thinner lamellae, a clear departure from the line (a) is observed. In Fig. 5, this trend is approximated by the line (c). Such a behavior indicates, that in the case of EO copolymers with big amount of hexyl branches, an increase of the transversal unit cell dimension occurs not only due to reduced crystal thickness but also because of some other reasons. Most probably, these are some additional stresses imparted on the basal surfaces of crystals by the branches residing in the interface between crystalline and amorphous phase.

In order to explain in which way the deformation of the unit cells localized in the surface layers of lamellae influences the average unit cell parameters *a* and *b*

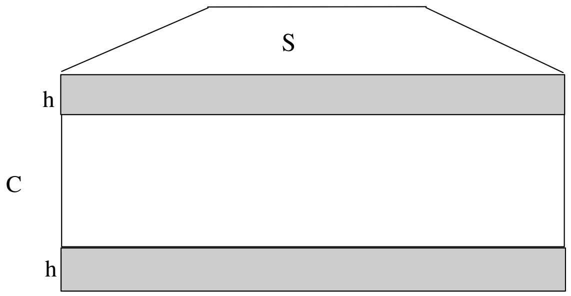

Fig. 6. A model of crystalline lamella.

measured in the experiment, one can consider a simplified model of lamella, which is shown in Fig. 6.

In this model, all unit cells contained in the lamella are divided into two groups: internal cells and surface cells. The thickness of layers in which deformed unit cells are localized is h and the thickness of lamella is C. The area of the basal surface of lamella is S. Let the average volume of the internal unit cell be $v_o = a_ob_oc_o$ and that one of the surface unit cell $v_s = a_sb_sc_s$.

The average unit cell volume measured in an X-ray diffraction experiment will be equal to:

$$v = xv_s + (1 - x)v_o \tag{3}$$

where x is a fraction of surface cells contained in the lamella,

$$x = \frac{2V_s}{V} = \frac{2Sh}{SC} = \frac{2h}{C} \tag{4}$$

where V is the volume of lamella and V_s is the surface layer volume.

Substituting x from Eq. (4) into the Eq. (3), one gets:

$$v = v_o + x(v_s - v_o) = v_o + \frac{2h}{C}(v_s - v_o) \tag{5}$$

and

$$abc = a_ob_oc_o + \frac{2h}{C}(a_sb_sc_s - a_ob_oc_o) \tag{6}$$

where a, b and c are the experimentally measured unit cell parameters. Because the length of c-edge is practically constant and does not depend on the branch content [10,14,16], one can transform the Eq. (6) to the new shape:

$$\frac{ab}{2} = \frac{a_ob_o}{2} + h(a_sb_s - a_ob_o)\left(\frac{1}{C}\right) = \frac{a_ob_o}{2} + D\left(\frac{1}{C}\right) \tag{7}$$

The last equation is fully consistent with the experimental formula of Davis et al. obtained for LPE and makes clear the linear dependence of ECCS on the reciprocal of the lamella thickness. As one can see, the slope D of this line is determined by the thickness h of the surface layer in which deformed unit cells are present and on the degree of their deformation: $(a_sb_s - a_ob_o)$. The intercept $a_ob_o/2$ is equal to average value of ECCS for the internal unit cells of lamella.

Based on the Eq. (7) one can interpret the experimental results obtained in this work for EO copolymers and compare them with the data of Howard and Crist [14] for EB copolymers.

In the case of EO copolymers with lower branch content and consequently thicker lamellae, both the degree of deformation of the surface unit cells as well as the thickness of the layers where they are localized, do not change considerably with lamella thickness. For this reason, the coefficient D is constant and the plot of ECCS versus (100/C) is linear. However, for higher branch content, the lamellae become thinner and thinner and the amount of branches crowded on the basal surfaces of lamellae increases. It is obvious, that in this case, the stresses imparted by the branches on the basal surfaces of lamellae are more pronounced and consequently the surface unit cells become more deformed. As a result, the coefficient D increases and the dependence (7) is not linear any more.

In EB copolymers (data of Howard and Crist), two mechanisms of unit cells deformation occur. One of them is the same as in the case of LPE and EO copolymers with low branch content. This is confirmed by the linearity of the considered plot (line (b)) and from nearly the same slope as in the case of line (a). The second mechanism is an inclusion of some small part of ethyl branches into the lamellar crystals. Such a conclusion results from a higher value of the intercept of the line (b). According to Eq. (7), the intercept is equal to ECCS of the internal unit cells. It means that the average volume of the internal unit cell in EB copolymers is bigger than in LPE.

For EB copolymers the range of lamella thickness for which the dependence (7) is linear, is clearly broader than in the case of EO copolymers (Fig. 5). This is because the ethyl branches are much shorter than hexyl ones and consequently the stresses imparted by them on the basal surfaces of lamellae are considerably smaller.

Taking into account that methyl branch is shorter than ethyl one, we can expect that also in EP copolymer two mechanisms of unit cells deformation occur. As one can see in Fig. 5, the ECCS value of EP copolymer is much bigger than that one of EB with similar thickness of lamella. It means that the inclusion of methyl branches into the crystalline structure occurs much more frequently than in the case of ethyl ones. This result is consistent with the literature data presented in the introduction. Of course, similarly as in LPE, EO and EB, the deformation of surface unit cells caused by a limited thickness of lamellae also takes place in EP. However, a comparison of the ECCS values for EP and EO with similar thickness of lamella (Fig. 5) indicates, that this mechanism is in EP less important than the branch inclusion.

Also the data shown in Fig. 3 confirm a partial inclusion of methyl branches in EP. In this figure one can see, that the average thickness of lamellae in EP is clearly higher than in EO copolymer with the same short branches content. As the hexyl branches are completely excluded from the crystals one can suppose, that the value of the thickness of lamella found for a given EO copolymer, is the maximum one that can be reached with a given average length of ethylene sequences and at a given crystallization conditions without including the side branches into the crystals. So, if the lamellae in EP copolymer are thicker they must contain methyl branches inside.

At the initial stage of heating, the unit cells of investigated materials expand with nearly the same thermal expansion coefficient, as it can be seen in Fig. 7. In this figure, a plot of the unit cell volume of LPE, which has been drawn according to the formula given by Swan [38] is also given for comparison. A small shift with respect to the data for the LPE sample investigated in the present work may result from different crystallization conditions (cooling rate). At higher temperatures, only EO1 and EO2 samples, with the smallest branch content, behave in the same way as LPE. In the case of remaining copolymers, some additional effects apart from the thermal expansion occur. To exclude the latter factor, the ratio of a copolymer unit cell volume at a given temperature to the volume of the unit cell of LPE at the same temperature, has been calculated and presented in Fig. 8.

Starting from about 50 °C, the relative volume of EP unit cell monotonically decreases with the temperature. On contrary, in the remaining copolymers it increases. The temperature at which the increase starts, is the lower, the higher the short branches content. Considerable changes occur also in the shape of the unit cells. Fig. 9 shows how the shape factor $k = a/b$ changes with the temperature. In Fig. 10, the relative shape factor i.e. the ratio of a copolymer shape factor to that one of LPE at the same temperature, is given. The plots from Figs. 7–10 related to EP sample clearly indicate, that at higher temperatures the unit cell of this copolymer becomes more and more similar to that one of LPE. In other words, an increasing temperature causes that it tends

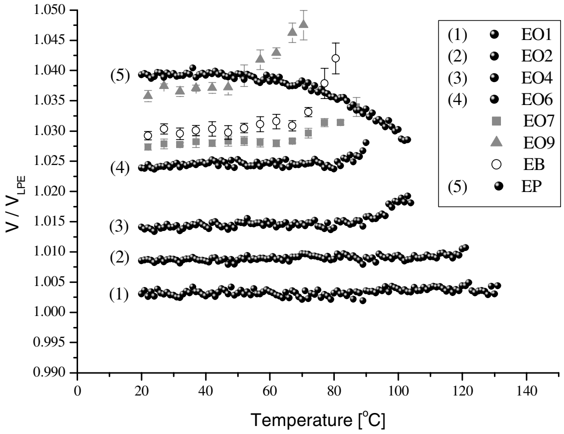

Fig. 8. Relative volume of a copolymer unit cell versus temperature. The relative volume V/V_{LPE} is the ratio of a copolymer unit cell volume at a given temperature to the volume of the unit cell of LPE at the same temperature. To reduce the noise, in the case EO7, EO9 and EB samples, the values were averaged over 5 data points and standard deviations were put on the plot as error bars.

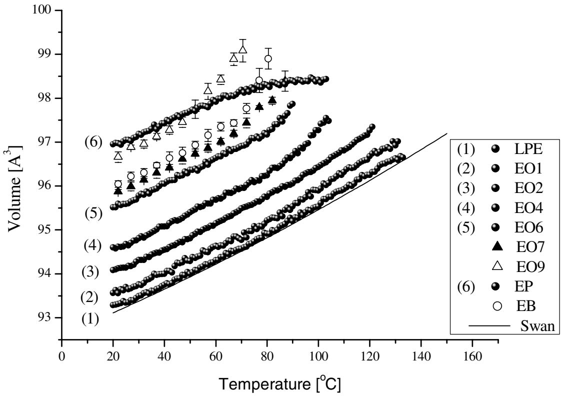

Fig. 7. Volume of the unit cell of investigated materials as a function of temperature. To reduce the noise, in the case EO7, EO9 and EB samples, the values were averaged over 5 data points and standard deviations were put on the plot as error bars.

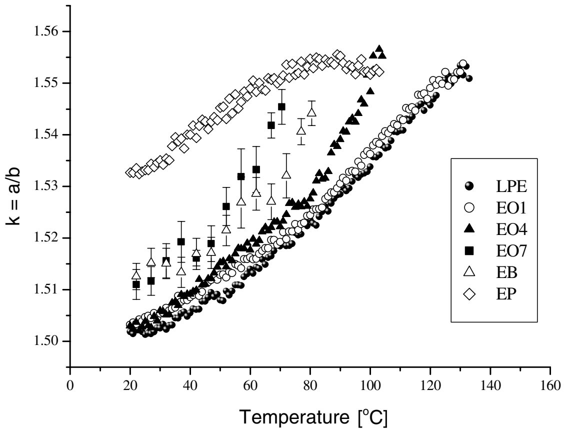

Fig. 9. Shape factor $k = a/b$ of the unit cell of selected copolymers as a function of temperature. In the case EO9 and EB samples, the values were averaged over 5 data points and standard deviations were put on the plot as error bars.

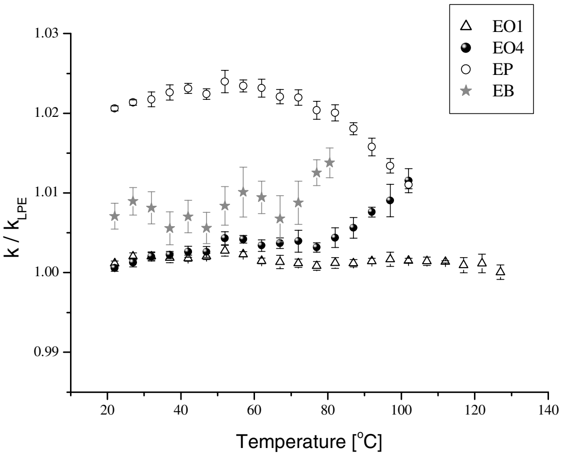

Fig. 10. Relative shape factor of a copolymer unit cell versus temperature. The relative shape factor k/k_{LPE} is the ratio of a copolymer unit cell shape parameter to that one of LPE at the same temperature. Presented values were averaged over 5 data points and standard deviations were put on the plot as error bars.

to the volume and shape of the LPE unit cell at high temperature. Most probably, thermal expansion results in such an increase of the EP unit cell volume, that included methyl branches have more free space inside. Moreover, the increase of the unit cell volume caused by included branch becomes smaller and smaller part of the thermally expanding unit cell volume. This phenomenon confirms once again a partial incorporation of methyl branches into the crystal structure.

In contrast to EP, the unit cell of EO copolymers becomes more and more deformed, starting from some characteristic temperature (Figs. 7–10). As there are no hexyl branches in the core of lamellar crystals, one can suppose that this extra deformation is caused by some thermally activated phenomena occurring in the regions of crystals localized near their basal surfaces. The results analyzed above and presented in Fig. 5 indicate, that already at room temperature, in the samples with high branch content, the unit cells located near the crystal surface are more deformed and have larger volume than these ones in the crystal core, because of the stresses imparted by excluded hexyl branches. Thermal expansion during heating causes that this volume still increases. At high temperature, increases also the mobility and conformational freedom of hexyl branches. Hence it is probable, that at some temperature, the volume of some surface cells will be large enough, to make possible a partial penetration of the end-parts of hexyl branches (i.e. methyl groups), residing near the crystals surface. Such a penetration must cause an additional increase of the average unit cell volume observed in the experiment. The temperature at which such a phenomenon can begin is the lower, the higher the "starting" volume of the surface unit cells i.e. the volume at room temperature. This would explain why the extra deformation starts at lower temperatures for copolymers with higher comonomer content. Such a phenomenon is also possible in the case of new crystals which appear during heating as a result of melting and recrystallization.

In EB sample, an increasing temperature influences the unit cell volume in the same way as in EO copolymers. Apparently, thermal expansion does not provide enough space to effectively diminish the unit cell deformation caused by incorporated branches, as it the case of EP copolymer. Besides, the fraction of ethyl branches included into the crystal core is much less than that of the methyl ones. For this reason, the increase of average unit cell volume is mostly determined by the deformation of unit cells located near the basal surfaces of lamellae. On can suppose, that the additional increase of the average unit cell volume which starts at about 70 °C, has similar sources as in the case of EO copolymers i.e. the penetration of ethyl branches located near the crystal surface into the surface cells enlarged by the thermal expansion.

In the temperature ranges for which the crystalline peaks 110 and 200 can be resolved in the WAXD patterns of investigated samples, the thickness of lamellae does not change considerably. The plot from Fig. 5, showing the effective chain cross section ECCS versus the reciprocal thickness of lamella 100/*C* at room temperature, has similar shape at higher temperatures. In Figs. 11–13, this plot is compared with the ones related

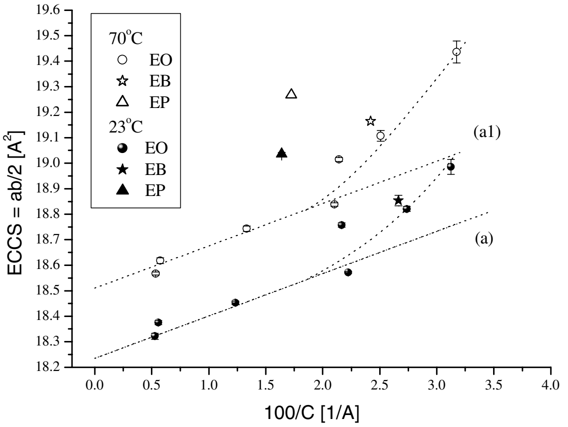

Fig. 11. A comparison of the plots of the effective chain cross section (ECCS) versus the reciprocal of lamella thickness at room temperature (23 °C) and at 70 °C. Presented values were averaged over 5 data points from the temperature range 21–25 °C and 68–72 °C respectively. Error bars represent the standard deviations. The error bars are not used when standard deviation is smaller than the size of symbols. Lines (a) and (a1) are described in the text.

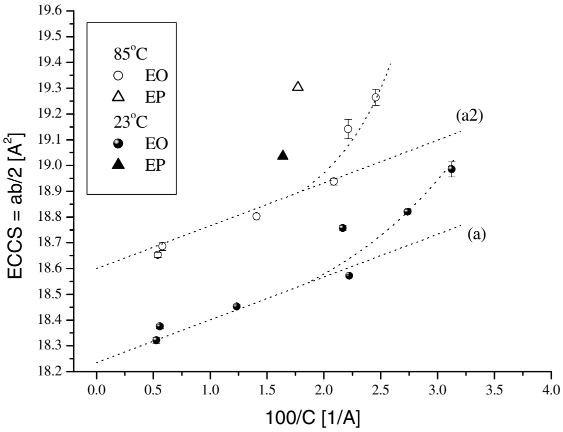

Fig. 12. A comparison of the plots of the effective chain cross section versus the reciprocal of the lamella thickness at room temperature (23 °C) and at 85 °C. Presented values were averaged over 5 data points from the temperature range 21–25 °C and 83–87 °C respectively. Error bars represent the standard deviations. The error bars are not used when standard deviation is smaller than the size of symbols. Lines (a) and (a2) are described in the text.

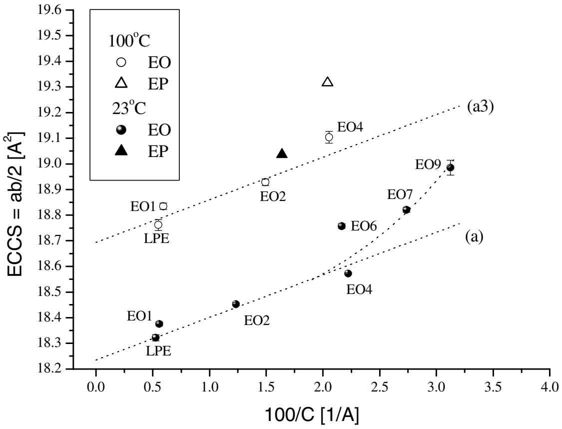

Fig. 13. A comparison of the plots of the chain cross section versus the reciprocal of the lamella thickness at room temperature (23 °C) and at 100 °C. Presented values were averaged over 5 data points from the temperature range 21–25 °C and 98–102 °C respectively. Error bars represent the standard deviations. The error bars are not used when standard deviation is smaller than the size of symbols. Lines (a) and (a3) are described in the text.

to 70 °C, 85 °C and 100 °C. The points represent the average values from the range 68–72 °C, 83–87 °C and 98–102 °C respectively.

Apart from the experimental data, the line (a), drawn according to the formula (2) of Davis et al. [23], and lines (a1), (a2) and (a3) are also shown. The latter lines were constructed by shifting the line (a) by factors resulting from the thermal expansion of the crystalline phase in LPE. These factors were calculated from the equation given by Swan [38] and used already in Fig. 7. As one can see, the values of ECCS for EO copolymers with the thicker lamellae, fits quite well to the lines (a1), (a2) and (a3). According to the Eq. (7), the same slope of these lines indicates, that in these samples, the degree of deformation of the unit cells localized near the basal surfaces of lamellae is the same as at room temperature. The ECCS values for the samples with higher branch content (EO6–EO9) are much higher than those indicated by the considered lines, similarly as it occurs at room temperature (Fig. 5). In the latter case, this was attributed to the stresses imparted by excluded hexyl branches on the crystals surface. However, the differences observed in Figs. 11 and 12 are clearly bigger than in the plot related to the room temperature. This fact is consistent with the extra deformation of the unit cell observed in Figs. 8–10, and assigned to the thermally activated penetration of the end-parts of hexyl branches into the surface cells, enlarged by the thermal expansion. As it is shown in these figures, such an effect occurs also for the sample EO4, starting above 85 °C. This explains a distinct shift of the point representing this sample in Fig. 13, above the line (a3) which is related to the temperature of 100 °C.

4. Conclusions

At room temperature, the dependence of the effective chain cross section on the reciprocal of the thickness of lamella in EO copolymers with moderate comonomer content (up to about 25 SCB/1000C), is the same as in LPE. This fact confirms, that no inclusion of hexyl branches into the crystal structure take place. The unit cell expands in the direction perpendicular to the chain axis due to reduced thickness of lamellae, caused by the presence of side branches which cannot be included into the crystal lattice. At higher hexyl branches content, an additional increase of the unit cell volume and change of its shape occur, because of the stresses imparted on the basal surfaces of crystals by the branches residing in the interface between crystalline and amorphous phase.

During the initial stage of heating, at lower temperatures, the crystalline phase of all investigated materials expands with nearly the same thermal expansion coefficient and the ratios of the unit cell volume in copolymers to the unit cell volume in linear polyethylene do not change. At higher temperatures, an extra expansion of the unit cell in EO copolymers with short branches content above 20 SCB/1000C, takes place. The temperature at which it begins is the lower, the higher the branch content. Most probably, this expansion is caused by a partial penetration of the end-parts of hexyl branches (i.e. methyl groups), residing near the crystals surface into the surface cells, enlarged by the thermal expansion. The linear dependence between the effective chain cross section and the reciprocal of crystal thickness, observed at room temperature for LPE and EO copolymers with low branch content, is preserved up to 100 °C. The same slope of respective plots indicates that the degree of deformation of the unit cells localized near the basal surfaces of lamellae is the same as at room temperature.

The effective chain cross section value determined for EB copolymer at room temperature agree with the data reported by Howard and Crist [14]. In EB copolymers some small part of ethyl branches is included into the crystal structure. However, the total increase of the average unit cell volume is mostly determined by the deformation of unit cells located near the basal surfaces of lamellae. The additional increase of the unit cell volume starting from about 70 °C, has probably similar sources as in the case of EO copolymers i.e. the penetration of ethyl branches located near the crystal surface into the surface cells enlarged by the thermal expansion.

The results obtained for EP copolymer fully confirm a partial inclusion of methyl branches into the crystal lattice. At room temperature, the thickness of lamellae in EP is higher and the unit cell is clearly bigger than those ones in EO copolymers with similar comonomer content. Much higher value of the effective chain cross section as compared with that one of EB copolymers indicates that the inclusion of methyl branches into the crystalline structure occurs much more frequently than in the case of ethyl ones. Additional strong confirmation have been obtained from the behavior at high temperatures. The increase of the EP unit cell volume resulting from the thermal expansion causes, that included methyl branches have more free space inside. The change of the unit cell volume caused by included branch becomes smaller and smaller part of the expanding unit cell volume. As a result, the relative (with respect to LPE) unit cell volume and the degree of its deformation decrease with temperature, tending to the volume and shape of the LPE unit cell at these thermal conditions.

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