

# On the $\alpha$ relaxation of the constrained amorphous phase in poly(ethylene)

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## Abstract

The idea of coexistence of two different amorphous fractions in semi-crystalline poly(ethylene) (PE) is taken into consideration. Differential scanning calorimetry, dynamic mechanical thermal analysis and positron annihilation were used to study the effect of supermolecular structure on the glass transition associated with ‘semi-ordered’ amorphous phase. The arrangement of chains, located in this phase, is forced internally by the presence of crystalline domains. Influence of drawing, irradiation and annealing on thermodynamic and structural parameters was investigated. In a series of experiments the correlation between the glass transition, the  $\alpha$  relaxation and the free volume of a semi-crystalline system was found. In order to better describe the relaxation, existence of two types of amorphous fractions was assumed. The relaxations are treated as a long-scale motion of macromolecule segments located into the ‘semi-ordered’ amorphous regions, or into the ‘real’ amorphous regions, and are labelled as  $\alpha_c$  and  $\alpha_g$ , respectively. The magnitudes of the loss peaks were quite sensitive to the free volume, which was found to increase by drawing and decrease by irradiation. Two different DSC traces were recorded for both glass transitions.

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## 1. Introduction

Polymeric crystals of sufficient size for detailed study are rare and thus little is known about single-crystal behaviour as a function of defect content. However, several authors postulated correlations between the defect structure and relaxation behaviour [1–3]. Details are not worked out because of lack of sufficient experimental information. The problem of better knowledge of crystal–amorphous interphase is still under consideration. The role of the interphase was already postulated (defined) by Flory in 1962 [4]. The internal

friction of poly(ethylene) of low density (PE-LD) was studied first in 1953 [5]. Later measurements exhibited, comparable to those of mechanical relaxation, three dielectric relaxations labelled,  $\gamma$ ,  $\beta$ ,  $\alpha$  [1–3]. However, the relaxation at the highest temperature ( $\alpha'$ ) was not observed. For the  $\gamma$  and  $\alpha$  the relaxations the values of the activation enthalpy were found as 46 kJ/mol and 105 kJ/mol, respectively. The enthalpy of the  $\beta$  process was determined mechanically as 159 kJ/mol, although other values (67–105 kJ/mol) were also published [1–3]. The  $\alpha'$  relaxation occurs at high temperature and can best be observed in creep experiments but only for the samples cast from solution. The used notation, i.e.  $\alpha$  and  $\alpha'$ , was introduced and explained in literature [1]. The  $\alpha'$  relaxation was found to be sensitive to thermal history of the specimen. The following hypothesis for the mechanism of the  $\alpha$  relaxation was postulated: the relaxation occurred due to reorientation motion within

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the crystals, concluded on the basis of NMR, X-ray and mechanical relaxation experiments [1,2,5–7]. The  $\alpha$  relaxation did not appear in PE-LD that had been quenched from melt to low temperature, i.e. for PE with low crystalline contents. If PE-LD was not quenched, then the  $\alpha$  peak was observed with a magnitude comparable to the  $\beta$  peak. It was established that the  $\alpha$  relaxation depends on both the degree of chain branching and the method of crystallisation [5]. Post-crystallisation annealing also played apparently a role for this relaxation [8–10]. It was shown that for poly(ethylene) the decrease in the relaxation modulus with rising temperature could not be explained only by changes in the degree of polymer crystallinity. The value of the modulus is thought to be related to the reorientation of crystallites in the amorphous matrix. According to some authors [1,2] the  $\alpha$  relaxation is due to the motion of  $\text{CH}_2$  units in the crystals, and the molecular mechanism is the same as the  $\gamma$  mechanism. It is generally accepted that the  $\gamma$  relaxation occurs due to the motion of  $\text{CH}_2$  units in the amorphous region. Therefore, according to the common opinion the same type of molecular movement (local mode) occurs for both  $\alpha$  and  $\gamma$  relaxations. In literature [1,2], it was proposed that the  $\alpha$  mechanism appeared due to the melting of the crystals (premelting), however, some authors questioned the melting explanation of this relaxation. Relaxations found in polymeric systems are strictly determined by the free volume, which may be estimated by dilatometric, X-ray or positron annihilation methods. Positron annihilation lifetime spectroscopy (PALS) is widely used for investigations of different aspects of polymer structures and positron behaviour in polymers [11,12].

It is commonly assumed that the properties of  $\alpha$  relaxation depend on crystal morphology. In our opinion, however, this hypothesis leaves the question undecided whether the  $\alpha$  relaxation in PE is due to either the molecular relaxation within the crystal phase or to the lamellar slip mechanism. We consider the  $\alpha$  relaxation in PE to take place in the interphase regions of the semi-crystalline structure. These regions are strongly perturbed by the presence of the lamellae, which stretch the polymer chains. It is easy to deduce, based on the model of paracrystallinity ([13] and references therein), that the chains building the amorphous phase in the bulk and in the interphase must exhibit different properties. The supermolecular structure of polyethylene was a subject of many papers. Although the concept of constrained amorphous phase was applied with success to other polymeric systems for many years [14,15], to our best knowledge, data concerning the  $\alpha$  relaxation in PE have been interpreted following conventional two-phase model [16,17]. The model assumed that the  $\alpha$  relaxation in PE occurred only in the defected crystal phase.

## 2. Experimental part

### 2.1. Sample preparation

Specimens were produced from granulated PE (Lupolen 2012 D schwarz 413, BASF) as a tape with a thickness of 1 mm and a width of 300 mm. The samples were divided into three parts: the first one unprocessed (*A*), the second one (*B*) drawn (40% elongation), and the third one (*C*) irradiated with high-energy electrons. The PE tapes were the same as used in a previous study [18]. The samples were cut from the tape, which had been prepared using the same procedure as rigorously as possible, and were additionally processed in our laboratory. A part of the samples was annealed at 150 °C over 1 h ( $A_a$ ,  $B_a$ ,  $C_a$ ) whereas other specimens were irradiated by a positron source over 24 h ( $A_p$ ,  $B_p$ ,  $C_p$ ). The positron-irradiated samples were used in calorimetric and mechanical studies. For mechanical studies bars of 250 mm length, 2 mm width and 1 mm thickness were cut down from all tapes. In order to study the effect of structure stability, the samples were stored at room temperature (20 °C) over four and ten months following sample preparation.

### 2.2. Methods

Thermal characterisation of the samples by DSC was performed by using a Perkin Elmer DSC7 instrument and the first heating run was analysed. In several cases other heating and cooling rates were also applied, as described in the discussion section. The melting temperature ( $T_m$ ) was defined as the minimum of the DSC endotherm. The enthalpy of melting ( $\Delta H_m$ ) was calculated from the area of the DSC peaks after a base line subtraction. It is obvious that the value of  $\Delta H_m$  strongly depends on the base line shape used. Therefore, the same type of sigmoidal base line was applied for all area calculations. The analyses were performed under following conditions: environment—nitrogen atmosphere; flow rate—20 ml/min; sample pan—aluminium, reference—empty aluminium pan; sample size—about 5 mg; heating rate—20 deg/min; calibration procedure—done with indium standard.

Dynamic mechanical thermal analysis was carried out with a Polymer Laboratories DMTA Mk III system. Loss tangent and  $E'$  curves were obtained in tensile mode. A frequency range between 0.01 and 300 Hz and the step heating regime within a temperature range from 20 to 120 °C were applied.

For the positron lifetime measurements a conventional slow-fast coincidence spectrometer with plastic scintillators was used [18]. Four exponential components were fitted to the measured spectra. The shortest component,  $\tau_1$  is related to the annihilation of parapositronium (*p*-Ps),  $\tau_2$  is attributed to the annihilation of the

free positrons and  $\tau_3$  describes the annihilation of orthopositronium (*o*-Ps) in crystallites. The component with longest lifetime,  $\tau_4$ , is attributed to the pick-off annihilation of *o*-Ps [11,12]. According to the model proposed by Tao [19] and Eldrup et al. [20], the component with the longest lifetime of the positron lifetime spectrum may be related to the mean radius of the free volume cavity,  $R$ , in the polymer matrix. The relative intensity of the *o*-Ps lifetime component,  $I_4$  is assumed to be proportional to the number of the free volume holes because it gives the information on the probability of *o*-Ps formation. Wang et al. [21] and Kobayashi et al. [22] proposed a semi-empirical relation which may be used for evaluation of the fractional free volume  $f$ . It is defined as

$$f = (V - V_0)/V = V_f/V \quad (1)$$

where  $V$  is the total macroscopic volume of the polymer,  $V_0$  is the volume occupied by molecules, and  $V_f$  is the free volume of the polymer. Wang et al. [21] and Kobayashi et al. [22] have proposed a semi-empirical equation which may be used to evaluate the fractional free volume,  $f$

$$f = A \times I_4 \times V_{\text{sph}} \quad (2)$$

where  $I_4$  is the relative intensity of the *o*-Ps lifetime component,  $V_{\text{sph}} = (4\pi \times R^3)/3$  is the free volume of the single hole (in nm<sup>3</sup>), the  $R$  value is taken from the lifetime measurements ( $\tau_4 = 0.5[1 - R/(R + 0.1656) + 1/(2\pi) \sin[2\pi R/(R + 0.1656)]]^{-1}$ ) and  $A$  is the normalisation constant. The  $A$  value was not measured in this work but as it is the constant the  $f$  value must be proportional to the product: ( $I_4 \times V_{\text{sph}}$ ).

### 3. Results and discussion

The transitions, relaxations and morphologies of branched and linear poly(ethylene) have been extensively examined by numerous investigators, and the results have been reviewed in books [1–3]. Because PE is a rather highly crystalline polymer, there is no doubt that the role of the crystal–amorphous interphase must be significant. This paper leads to a broader understanding of the relationship between processing history and morphology of the interphase in the PE products. A wide range of conditions applied for the material preparation made it possible to obtain specimens of different morphology resulting from various arrangements of the macromolecules. The calorimetric and structural results are summarised in Table 1. Data clearly indicate a correlation between the condition of preparation and the PE crystallinity. The crystalline content could be estimated from the endothermic area of each DSC trace taking 140 J/g as the value of heat fusion for the 100% crystalline polymer [23]. However, this value have to be used with caution because other values can be found in literature. One broad peak was usually recorded when the DSC investigations were performed with a heating rate of 20 deg/min. However, it was possible to perform the analysis under such conditions that the broad endotherm could be separated into three recognisable endotherms. This problem, however, will be discussed in the last part of the section. When the samples were stored at room temperature over four months (and longer [18]), the  $\Delta H_m$  values decreased, exhibiting a different degree of crystal phase damage. This effect is labelled as a ‘ $d$ ’ parameter in Table 1. The parameter was calculated as a quotient of the melting enthalpy of the stored sample and the as-produced sample, respectively. The values in Table 1 are given in percentage. It must be emphasised that the  $\Delta H_m$  values of stored samples were

Table 1

Thermodynamic and structure parameters of samples studied by DSC (first run with the heating rate of 20 deg/min) and positron annihilation:  $\Delta H_m$ —enthalpy of melting;  $d$ —parameter of the crystalline phase destruction;  $R$ —mean radius of the spherical well (the measurement error is 0.002 nm);  $I_4$ —relative intensity of the *o*-Ps lifetime component;  $f$ —fractional free volume

Sample	$\Delta H_m$ [J/g]	$d$ [%]	$R$ [nm]	$I_4$ [%]	$f$ [a.u.]
<i>A</i>	81.0	37.9	0.333	21.9 ± 0.5	1.00 ± 0.03
<i>A<sub>a</sub></i>	90.3	37.2	0.333	21.8 ± 0.7	0.99 ± 0.04
<i>A<sub>p</sub></i>	69.6	26.0	—	—	—
<i>B</i>	71.9	25.4	0.335	21.6 ± 0.5	1.00 ± 0.02
<i>B<sub>a</sub></i>	80.1	16.3	0.336	21.80.5	1.01 ± 0.03
<i>B<sub>p</sub></i>	66.4	18.4	—	—	—
<i>C</i>	78.8	26.9	0.330	19.9 ± 0.4	1.00 ± 0.03
<i>C<sub>a</sub></i>	68.5	12.8	0.333	22.4 ± 0.6	1.16 ± 0.03
<i>C<sub>p</sub></i>	77.8	28.4	—	—	—

The blank spaces for the *A<sub>p</sub>*, *B<sub>p</sub>* and *C<sub>p</sub>* samples mean that the sample was not studied by the positron annihilation after the first positrons irradiation (for explanation see experimental part).

nearly the same and ranged in the vicinity of 55 J/g (only the value of  $B_a$  was about 67 J/g). Hence, only values of the  $I_4$ ,  $R$  and  $f$  parameters are correlated with the arrangement of the chains in the amorphous structure; the corresponding values are listed in Table 1. The  $f$  values for the non-annealed samples were taken, for three types of samples, as reference values. It is accepted that  $\tau_4$  is proportional to the overlap of the positron and electron wave functions in a free volume cavity [19,20]. Thus the value of  $\tau_4$  correlates with the dimension of the cavity that is reflected in the  $R$  value. Almost constant values of  $R$  suggest that the dimensions of these cavities did not change drastically for the three different types of the samples (A–C). Since the  $R$  values for the  $B$  and  $B_a$  samples are the highest, the mobility of the chains in the amorphous regions of these samples should be the highest. The behaviour of the  $f$  values for the samples types  $A$  and  $B$  would suggest that the supermolecular structure of the polymer (the way of packing of the macromolecules in a condensed state [24,25]) was resistant to the annealing in both cases. On the contrary, the  $f$  value for the  $C$  samples increased after annealing. It seems that for the irradiated samples the number of the free volume holes increased, as  $I_4$  is proportional to this number. The increase is not significant as it is seen from Table 1. At the moment it is difficult to explain this behaviour. Likely, the high energy electron irradiation degraded the samples and produced some defects which created new cavities during annealing [1,2,26]. To explain this problem, further measurements are in progress.

Although the  $T_g$  value for PE is still disputed (this value depends on the measurement techniques: calorimetric, dilatometric, mechanical or dielectric spectroscopies, and the definition of the vitrification process), in our opinion, the glass transition should be located in a low temperature range. Three temperatures (found in the DSC traces) were taken into consideration as possible  $T_g$  option:  $-120$ ;  $-50$  and  $20$  °C [2,23,27]. The lowest temperature ( $-120$  °C) seems to be sufficient for the large-scale mobility of the macromolecule fragments located within the ‘real’ amorphous regions. However, the problem of the glass transition in PE is strictly related to the basic question concerning the  $T_g$  definition for the glass forming substances [28–31].

There is experimental evidence, which should be reviewed, proving the existence of two fractions of the amorphous phase. The first fraction refers to features of the ‘real’ amorphous phase whereas the second fraction is related to the constrained amorphous phase. Hence, the structural relaxation (micro-Brownian motion, very often labelled as  $\alpha$  relaxation) should also be separated into two different motions of polymer chains, which would be located either within the ‘real’ amorphous phase or within the ‘semi-ordered’ amorphous phase, respectively. According to this model, it was suggested to label  $\alpha_g$  as pure amorphous relaxation and  $\alpha_c$  be-

longing to the ‘semi-ordered’ amorphous phase. DSC traces also indicated the possibility of this assignment [32,33]. In the case of PE-LD two glass transitions are observed at  $-120$  °C and  $20$  °C, respectively. The first transition, i.e. at lower  $T_g$ , concerns the undisturbed amorphous regions which exhibits properties and thermodynamic parameters (e.g.  $T_g$ ,  $\Delta C_p(T_g)$ ) identical to those of the bulky amorphous polymer. The second transition concerns the regions disturbed by the presence of the lamellae and exhibit the higher  $T_g$  value. The second glass transition, e.g. the one that one can find in Fig. 1 for the  $B$  sample, was overlapped with the DSC peak giving one endotherm with the changed base line before and after the transition. The presentation of chosen DSC curves is restricted to the temperature range of the second glass transition, hence, the  $\alpha_c$  relaxation. The position of the glass transition in a temperature scale varies reflecting the sample preparation. Only the heating run for sample  $B$  exhibits the step-wise transition just before the peak. It is generally accepted that such a situation takes place when an additional order in the amorphous phase is introduced [34,35]. Such order could be a result of the drawing process, which stretched the amorphous regions additionally.

Let us assume that the value of  $\Delta H_m$  given in Table 1 reveals the amount of crystalline phase in the specimen and the temperature of the glass transition of the ‘semi-ordered’ amorphous phase might be influenced by the number of crystallites. This would mean, that the larger the amount of the crystalline phase the higher the temperature of the second glass transition. The following temperatures for the onset and the endset of the transition and enthalpies were found for the samples:  $A$ — $80.0$ – $85.5$  °C,  $\Delta H = 0.5$  J/g;  $C$ — $72.5$ – $78.5$  °C,  $\Delta H = 0.2$  J/g;  $B$ — $57.2$ – $68.6$  °C,  $\Delta H = 0.2$  J/g. It is easier to rec-

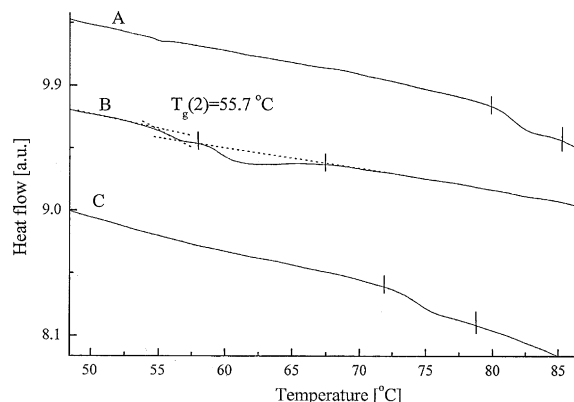


Fig. 1. DSC curves, recorded during the first heating runs, were performed at heating rates of 20 deg/min, for the samples  $A$ ,  $B$  and  $C$ . The onset and the endset of the first endotherm are shown. The temperature of the step-wise transition for the  $B$  sample is also labelled.

ognise a peak or a jump in a DSC trace if we take into consideration the first derivative of  $C_p \rightarrow f(T)$ .

The study of internal friction of PE-LD exhibited several relaxations [1,2]. For samples prepared from a melt three relaxations labelled  $\gamma$ ,  $\beta$ ,  $\alpha$  were revealed by mechanical spectroscopy. The  $\alpha'$ -mechanism was found additionally for PE cast from solution. Although the  $\alpha$  relaxation was attributed to crystalline regions, the correlation between the change of the crystallinity and the decrease of moduli was not discussed in detail. In this paper only one of them, labelled  $\alpha$ , is discussed. The  $\alpha$  relaxation is labelled in this paper as  $\alpha_c$  relaxation and the  $\gamma$  relaxation is labelled as  $\alpha_g$  relaxation that corresponds with our previous papers [32,33]. The temperature dependence of the storage modulus  $E'$  and the value of  $\tan \delta_E$  of the  $\alpha$  relaxation at the frequency of 3 Hz for PE-LD is shown in Fig. 2a and b, respectively. The effect of annealing on the loss modulus presented in Fig. 2b shows that the observed maximum broadens and diminishes in amplitude. It can be seen that both the magnitude of the  $\alpha$  peak and its relaxation time,  $\tau = (2\pi f_{\max})^{-1}$ , depend on thermal history (Fig. 2c). The enthalpies of activation,  $\Delta H_z$ , were calculated from Arrhenius fits to the data. It must be emphasised that dielectric and mechanical data ( $\log(\tau) \rightarrow f(1/T)$ ) for  $\alpha$  relaxations [1,2], can be fitted either by the Vogel–Fulcher relationship or, as it was done in this case, by an Arrhenius plot. However, the latter is always typical for the thermally activated process and is observed in a temperature range far from the glass transition zone of polymer. The former is adequate for the relaxation, which can be related to a step-wise transition in the DSC curve [30–32,36,37]. In our opinion, both mathematical formulae might reveal the same behaviour of chains located in various amorphous structures. The activation enthalpies, together with the parameters taken from the mechanical spectra, are presented in Table 2.

The samples  $A_p$  and  $B$  were brought to essentially the same crystallinity by two different routes. The intensity of the  $\alpha$  peak ( $\tan \delta_E$ ) is much smaller for the specimen that was irradiated by the positron beam ( $A_p$ ) than for the drawn one ( $B$ ). Also,  $\Delta H_z$  values are slightly different for these samples. Similarly, lack of correlation between  $\Delta H_m$  and the relaxation parameters can be observed for  $A$ ,  $B_a$  and  $C$  samples. Three different enthalpies of activation were found though the number of crystallites is nearly the same. However, in the case of the samples mentioned above,  $\tan \delta_E$  of the  $\alpha$  relaxation looks quite similar for these samples. The lowest  $\Delta H_z$  value was obtained for the  $A$  sample cast from the melt. It means that the molecular motion is less restricted as compared with all other samples under investigation. The restriction in the segments fluidity increased somewhat following sample irradiation by positrons ( $A_p$ ). The radiation induces cross-linking [1,2,26], which restricts large-scale mobility, on the one hand, and decrease the

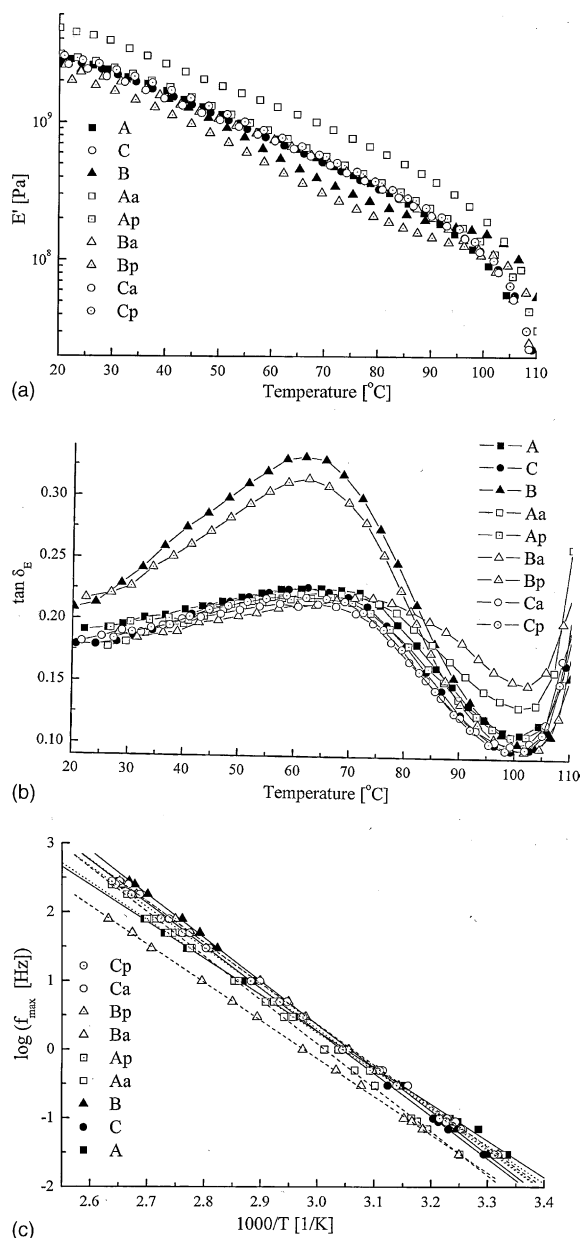


Fig. 2. (a) Temperature dependence of the storage modulus  $E'$  at 3 Hz for the PE samples prepared under different conditions. The same symbols, as labelled in Tables 1 and 2, were used. (b) Temperature dependence of the loss tangent at 3 Hz for the PE samples prepared under different conditions. (c) Arrhenius plot of the  $\alpha_c$  relaxation for PE samples prepared under different conditions. The data for the unprocessed samples ( $A$ – $C$ ) are fitted by the solid lines. The dashed and dotted lines represent the fitting for the annealed samples ( $A_a$ ,  $B_a$ ,  $C_a$ ) and the positron irradiated samples ( $A_p$ ,  $B_p$ ,  $C_p$ ), respectively.

amount of fraction taking part in the  $\alpha_c$  relaxation, on the other hand. The activation enthalpy increases but

Table 2

Parameters of mechanical studies taken from the curves measured at 3 Hz:  $\Delta H_x$ —enthalpy of activation

Sample	$\tan \delta_{\max(3\text{Hz})} \cdot 10^2$	$T_{\max(3\text{Hz})}$ [°C]	$E'_{20}$ [Pa · 10 <sup>-9</sup> ]	$E'_{100}$ [Pa · 10 <sup>-8</sup> ]	$\Delta H_x$ [kJ/mol]
<i>A</i>	22.58	64.7	2.85	0.99	101.6 ± 0.4
<i>A<sub>a</sub></i>	22.19	66.3	4.84	1.93	122.4 ± 0.6
<i>A<sub>p</sub></i>	22.00	65.0	3.08	1.27	104.8 ± 0.6
<i>B</i>	33.32	62.0	2.66	1.70	120.7 ± 0.4
<i>B<sub>a</sub></i>	21.92	73.9	2.54	0.98	106.2 ± 0.2
<i>B<sub>p</sub></i>	31.58	62.0	2.05	1.21	114.9 ± 0.5
<i>C</i>	22.67	61.7	2.86	1.18	118.6 ± 0.5
<i>C<sub>a</sub></i>	21.42	61.7	2.61	1.13	113.8 ± 0.7
<i>C<sub>p</sub></i>	21.92	61.3	3.01	1.27	112.8 ± 0.5

The values  $E'_{20}$  and  $E'_{100}$  were pointed out at 20 and 100 °C respectively.

the maximum of  $\tan \delta_E$  decreases. The annealing gives nearly the same result (*A<sub>a</sub>*). However, the tendency is stronger for the  $\Delta H_x$  value and the enthalpy increase is larger (the highest value for all studied specimens) in this case. Most likely, this behaviour is due to the increase of the number of the crystals. The larger the number of the perfect crystals the more strained the chains in the 'semi-ordered' amorphous regions, which are located into the interphase area. A similar effect was observed earlier for other polyolefins [38,39]. The authors suppose that if a correlation between the number of crystals and the strain is present, the  $\alpha_c$  relaxation for the polymer with higher degree of crystallinity, e.g. PE-HD will diminish. We can see that the maximum of  $\tan \delta_E$  is shifted towards higher temperature (about 2 °C for the annealed sample *A<sub>a</sub>*). While the annealing of the unprocessed polymer, *A<sub>a</sub>*, increases  $\Delta H_x$ , for the drawn or irradiated polymer samples, *B<sub>a</sub>* and *C<sub>a</sub>*, some decrease of the activation enthalpy is observed.

As is shown in Table 1 the number of crystallites for the samples *A* and *C* is comparable and for the *B* sample is distinctly lower. Since the  $\alpha_c$  relaxation is activated with various enthalpies for these three specimens, their supermolecular structures must be different. The higher enthalpy means that the motion is more restricted, likely, due to additional strain caused by the external drawing. Also, a large number of amorphous regions must exist in the *B* sample because one of the lowest amounts of the crystalline phase was pointed out from the DSC measurements. The question is whether the amorphous regions exhibit homogeneity of their supermolecular structure and whether the chains located in various amorphous regions exhibit different mobilities? Because the *B* sample was drawn, the amorphous region must be more or less ordered that might implicate some restriction. This fact is revealed by one of the highest activation enthalpy observed for the corresponding specimen. The maximum of  $\tan \delta_E$  reflects the amount of this phase, which would have to be the largest. A similar effect for PE-LD can be observed when the unprocessed

sample was annealed (*A<sub>a</sub>*). The enthalpy is the highest with regard to all samples but the maximum of  $\tan \delta_E$  is one of the lowest. We believe that annealing causes additional arrangement of the amorphous regions but simultaneously decreases the amount of this phase due to secondary crystallisation. One can see in Table 2 that the highest activation enthalpies (118.6 kJ/mol, 120.7 kJ/mol and 122.4 kJ/mol) would be found for the specimens prepared under quite different conditions. This means that different supermolecular structures of the interphase areas were created in corresponding specimens. In the case of the irradiated sample (*C*) the restriction results form the cross-linking while for the annealed (*A<sub>a</sub>*) and drawn (*B*) samples reveals the bigger number of lamellae and the better order of chains, respectively. Therefore it is postulated that the existence of the 'semi-ordered' amorphous fraction in polymeric materials is a consequence of the internal stretching. As long as the crystallinity of a sample is relatively low, the crystallites might be treated as cross-links and rigid filler in an amorphous matrix. With decreasing crystallinity the amount of regions stretched by the crystal decreases and the viscoelastic behaviour resembles more and more that of a cross-linked network.

The melting process, recorded in the DSC measurements as a broad peak with two local minima, was separated into three peaks when the heating rate was 1 deg/min. Such a distinct separation was only possible for the materials stored over ten months. A comparison of two DSC curves obtained with the different heating rates is presented in Fig. 3. When the heating rate was increased (from 1 deg/min to 20 deg/min) the minimum of the second and third peaks shifted towards high temperatures by about 7.5 and 20.5 °C, respectively. However, the first peak shifted towards low temperatures by about 18 °C that exhibited the reorientation process, opposite to the shift in the melting transitions revealed by the second and the third peaks. The beginning of melting, extrapolated from the DSC trace at 1 deg/min as the onset of the both endotherms, are located at 105

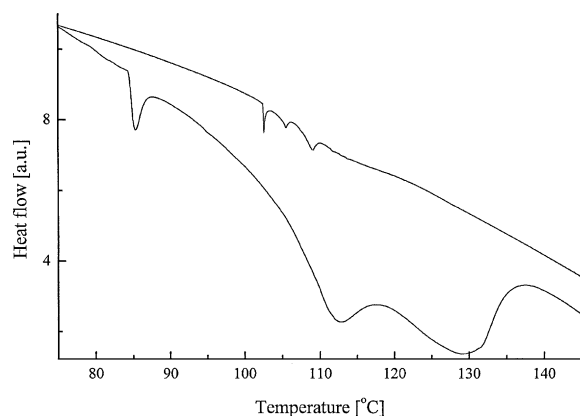


Fig. 3. Raw DSC curves recorded at a heating rate of 1 deg/min (upper curve) and at 20 deg/min (lower curve) for the stored sample. The data were not corrected for the mass of the samples.

°C and 107 °C, respectively. The first value exhibits good correlation with the temperature of the drastic decrease of the storage moduli  $E'$ . The values of  $E'$  at 100 °C are given in Table 2. The position of the first endotherm exhibits a correlation with the positions of the  $\alpha$  relaxation, denoted in this paper as  $\alpha_c$ .

#### 4. Conclusion

The problem of the origin of the  $\alpha$  relaxation was investigated for PE-LD. The facts presented in this paper, i.e., the low enthalpy of activation, the Arrhenius relationship and the DSC traces, indicate that the relaxation labelled in literature as the  $\alpha$  relaxation refers to the large-scale motion of the macromolecular segments located within the amorphous regions. However, the chain arrangement in these regions are affected by the presence of crystallites. Different processes, i.e. annealing, drawing or irradiation by electrons or positrons, can restrict the mobility of the chains within these regions. The features of such constrained domains differ from the feature of unconstrained amorphous regions, which exhibited similar behaviour as the amorphous phase of bulk polymers. The orientation induced by the presence of lamellae results in the appearance of the constrained amorphous structures for PE-LD. Therefore, in order to give a better description of relaxation, two types of amorphous fractions should be distinguished. The  $\alpha$  relaxation should be treated as a long-scale motion of macromolecule segments located within the 'semi-ordered' amorphous regions,  $\alpha_c$ , or within the 'real' amorphous regions,  $\alpha_g$ . The magnitudes of the loss peaks are quite sensitive to the free volume, which increases by drawing and decreases by irradiation. Unfortunately, a precise correlation between the mechanical spectrum and the

free volume of both amorphous fractions cannot be given at present. Most likely, it is due to the usual computational procedures of free volume calculations used. The procedure assumes four decaying components, however, it includes only the one suitable for the amorphous phase. Better correlation should be achieved if we assume the existence of two amorphous regions. This means that five components in the procedure must be considered. In this case the assumption of spherically shaped free volume should also be lifted. The molecular motion related to  $\alpha_c$  relaxation might be treated as a precursor for melting transition.

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