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Relaxation Processes in Polymer Surface Layers

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Summary: A recently built and patented device Nanoluminograph is used for the investigation of the relaxation processes in the surface layers of HDPE films, produced at various conditions. The work of the device is based on the phenomenon of radiothermoluminescence. The use of high-frequency low-power, low-temperature plasma as an ionizing source, and a reduction of the consumed energy down to several orders of magnitude (as compared to that used in similar devices) provides excitation of a surface layer as thin as 100–200 nm. The high sensitivity of the device enables one to reduce the excitation time to 1–2 seconds for obtaining a sufficient intensity of glow curves even from ultrathin layers 20–30 nm thick. All of that minimizes the modifying plasma action on the samples under investigation and provides well reproducible and reliable data. It is found that the intensity, number and positions of peaks on the glow curves are strongly influenced by the preparation conditions of polymer films. The complicated profile of glow curve peaks allows one to assume the overlapping of multiple relaxation processes. Decomposing and fitting peak profiles with the help of a PEAKFIT computer program result in revealing at least 4 relaxation transitions in the temperature region from 109 to 213 K. The temperatures and activation energies of relaxation transitions in surface layers appeared to be lower than those inferred from the DSC data for the bulk polymer. The activation energies of trap depletion upon heating are calculated. The nature of traps is discussed in terms of molecular conformations, morphology and structural defects, as well as the attribution of the observed relaxation transitions to defreezing mobility of different kinetic units.

Keywords: activation energy; molecular motion; radiothermoluminescence; relaxation transitions; surface properties

Introduction

The understanding of surface properties is of great importance because the behavior of bulk materials depends dramatically on the properties of surface and pre-surface layers. It is the surface, which controls the behavior of solids in various media and in the field of various forces at the great extent. The knowledge of a surface condition opens a route to the scientifically-based surface modification aiming at the production of the materials with the desirable optical, mechanical, adhesive, luminescent and other properties.

There are a number of modern devices providing information about the surface of solids, such as XPS, SEM, AFM a o. All of them have their advantages and drawbacks.

A new device enabling surface investigations is Nanoluminograph [1]. Its work is based on a well-known phenomenon of radiothermoluminescence [2,3].

In contrast to the conventional devices using thermoluminescence for the analysis of materials exciting by X-ray or γ-quanta,

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the activation of a sample in Nanoluminograph is carried out by high-frequency low-power, low-temperature plasma, the activation time and consumed power being minimal. It allows one to investigate the relaxation and phase transitions in thin surface layers of solids (100–300 nm). This unique device can be then considered as a "surface DSC".

It is used in the present work for a study of the relaxation transitions in the surface layers of melt-crystallized HDPE. The aim of this investigation was, first, to clarify whether there is a difference between characteristics of relaxation transitions on a surface (inferred from Nanoluminograph glow curves) and in the bulk (inferred from DSC data), and, second, to understand better the nature of electron traps. The molecular mechanisms responsible for depletion of the traps were also studied.

Experimental Section

Samples

Compression-moulded films (100 μm thick) were formed from the reactor powder of HDPE (Moplen, $M_w = 170{,}000$ g/mol). The HDPE was compressed at 170 °C for a period of 1 min at a pressure of 12 MPa between two heated stainless steel discs and two separating Al foils of 25 μm thick. The sandwiches consisting of Al foils and melted HDPE were taken out from an oven and immediately submerged in a melting acetone ($T_m = -95\,^\circ C$) (PE-I) or were slowly cooled down in the oven (PE-II). The cooling rate is approximately 7 °C/min.

Thermoluminescence Study

The scheme of Nanoluminograph manufactured by PlasmaChem GmbH (Germany) is presented in Fig. 1.

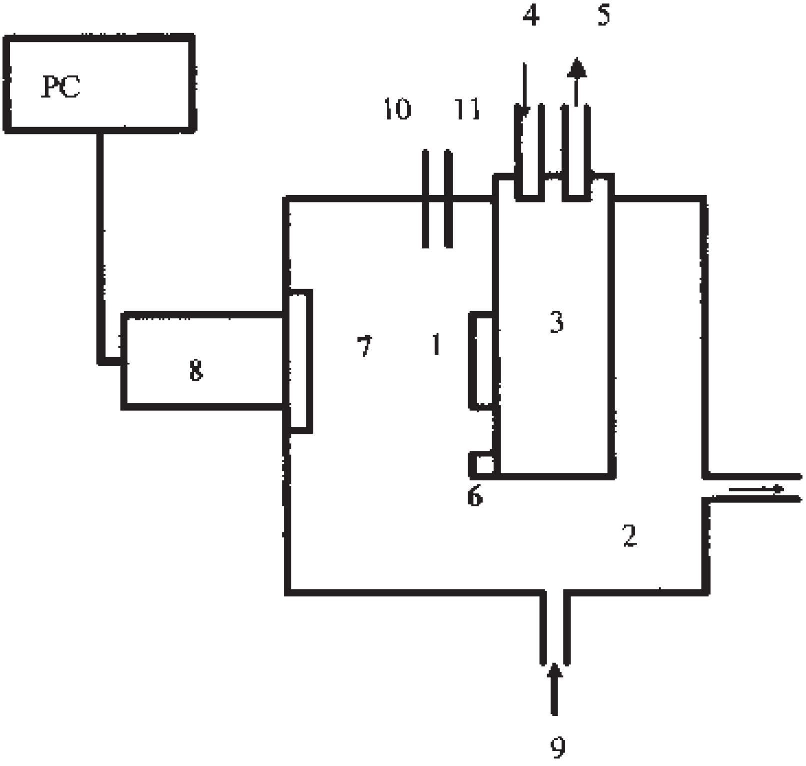

Figure 1.
The scheme of Nanoluminograph.

A film sample (1) put in a Nanoluminograph vacuum chamber (2) is attached to a sample holder (3) made in a form of a hollow copper cylinder with a passage (4) for filling it by liquid nitrogen. Another passage (5) is done for an exit of nitrogen vapours upon heating the sample holder. A stream of pre-heated nitrogen, which is pumped out from a Dewar vessel and passes through an oven, heats the holder. The sample temperature is measured by a thermoresistor (6) fixed to the cylinder next to a sample. The chamber is equipped by a quartz window (7) and by a photomultiplier (8), which is located outside the chamber. The chamber is evacuated down to a pressure of $1.33 \cdot 10^{-5}$ Pa, the hollow cylinder is filled by liquid nitrogen and the sample is cooled. Argon is then fed through a leak (9) to the chamber to a pressure of about 13.3 Pa, and a trigger (10) ignites a glow discharge, which is sustained by a high-frequency (13.6 MHz) generator (11) for a desirable period of time (usually about 1 s). A screen closes the window during the discharge to prevent the overloading of a photomultiplier. When the generator is switched off, the screen is removed, and an output signal from the photomultiplier comes to PC data collecting bus. The plasma power was as low as $10^{-3} - 10^{-4}$ Wt/cm^3 of plasma.

First, the isothermal thermoluminescence is observed during relatively long time. The oven for heating the sample is only switched on when the intensity of isothermal luminescence falls down to the level of a photomultiplier noise as it is shown in Fig. 2. The heating rate may vary from 3 to 20 K/min.

FTIR-ATR Study

IR spectroscopy was used to reveal a possible modification of surface layers of the samples under investigations, namely, formation of cross-links or molecular scissions in a surface layer of the samples exposed to the action of glow discharge upon the investigation in Nanoluminograph. The spectra from the HDPE films activated by Ar plasma for a period of 10 and 31 sec were recorded on a Bruker IFS-88 IR-spectrometer in the FTIR-ATR mode in the range from 700 to 1400 cm^{-1}.

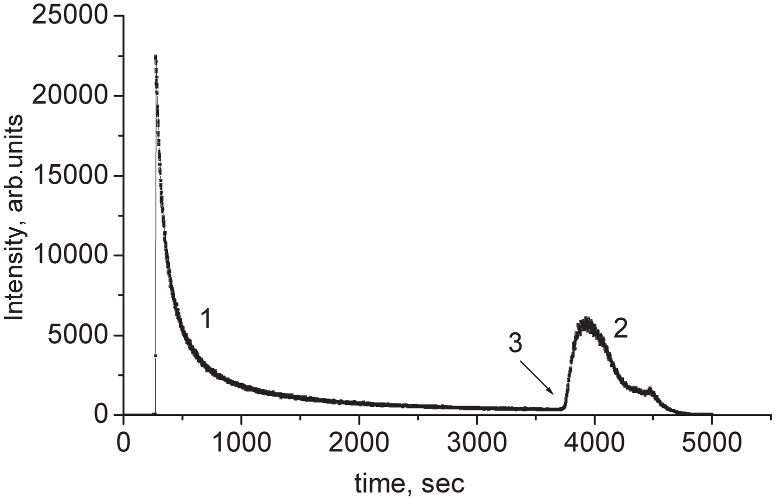

Figure 2.
Isothermal luminescence at liquid nitrogen temperature from frozen PE film after its activation by high-frequency low-temperature Ar plasma during 1 s at a pressure of 13.33 Pa (1), and a thermoluminescence upon heating the film at a rate of 10K/min (2). The moment of the switching on the heating of a sample is indicated by an arrow (3).

Results and Discussion

A Study of Calibrated Layers

In order to estimate the thickness of the analyzed surface layer, the glow curves were recorded from a number of calibrated plasma-polymerized methane layers on Cu foils (10 μm thick) especially prepared and kindly supplied by PlasmaChem GmbH. The thickness of the layers varied from 2.5 to 595.8 nm. Two peaks were observed on the glow curves from the layers. Their intensity first increases with increasing thickness and then goes to saturation. The intensity reaches saturation for the samples of 300–400 nm thick, which allows one to suggest that using Nanoluminograph we analyze surface layers of this thickness. However, a layer of 50–100 nm thick mostly contributes to the observed intensity.

FTIR-ATR Study of Plasma-Activated PE Films

The absorption of plasma energy by a polymer may modify a thin surface polymer layer. The plasma-chemical reactions occurring in it can result in molecular scission, in branching or cross-linking molecules, in the formation of double bonds and end groups in dependence on a nature of the plasma-forming gas and plasma conditions [4–7].

The attention was made to the possible appearance (or a change in the intensity) of the absorption bands at 888 cm^{-1} (rocking vibrations of CH$_2$–groups in vinylene RR'C=CH$_2$ bonds), at 908 cm^{-1}(rocking vibrations of CH$_2$ groups in vinylidene (RCH=CH$_2$) bonds), at 964 cm^1 (rocking vibrations of CH groups in trans-vinylene sequences (RCH=CHR$'$)), at 990 cm^1 (rocking vibrations in CHRCH=CH$_2$ groups), at 1380 cm^{-1} (vibrations of the methylene groups) and at 1720 cm^{-1} (C=O groups).

No traces of cross-links or molecular scissions in the PE films exposed to the action of glow discharge in argon atmosphere (even for a period exceeding the usual exposure time by a factor of 30) are detected in the frame of sensitivity of the Bruker IFS-88 spectrometer. The C=O bonds are also not revealed. This shows that Nanoluminograph is the unique equipment allowing one to study actually the true structure of a polymer surface.

A Study of Melt-Crystallized HDPE

Fig. 3 represents the glow curves from HDPE films, quenched in a melting acetone (PE-I) and slowly crystallized during cooling in the oven (PE-II). The duration of glow discharge in argon was 1 s. For comparison, the glow curve of the PE-II film activated for a period of 0.1 s is also given. Two low-temperature peaks are observed on the glow curves for both samples in the region 110–250K, the luminescence intensity being much higher for PE-I (Fig. 3, curve 1). The glow curve intensity decreases with reduction of activation time (Fig. 3, curve 3). Any luminescence is not detected at higher temperature in our experiments.

As known, the peak appearance on the glow curves is associated with the recombination of the stabilized charge carriers in the temperature range of relaxation transitions due to release of molecular mobility in the immediate vicinity of the charge traps, which can be of different nature and depth [2,3]. The absence of the luminescence at higher temperature suggests that only shallow traps could be filled in the samples activated in the chosen conditions. It was shown that only high dose rate / high-absorbed dose allows one to observe luminescence in the 300–400K-temperature range [8]. We especially did not do it to avoid modification effect of plasma treatment and to study a native polymer surface.

The complicated profile of glow curve peaks makes us to suggest the overlapping of the several ''elementary'' relaxation processes occurring at the close temperatures. We decomposed the experimental peaks into elementary ones with the help of the computer program PEAKFIT.

The fitting of experimental curves by a number of elementary peaks is a voluntary procedure to some extent. At least one should have to assume a character of a peak profile.

As follows from the theoretical considerations, a type of glow kinetics controls

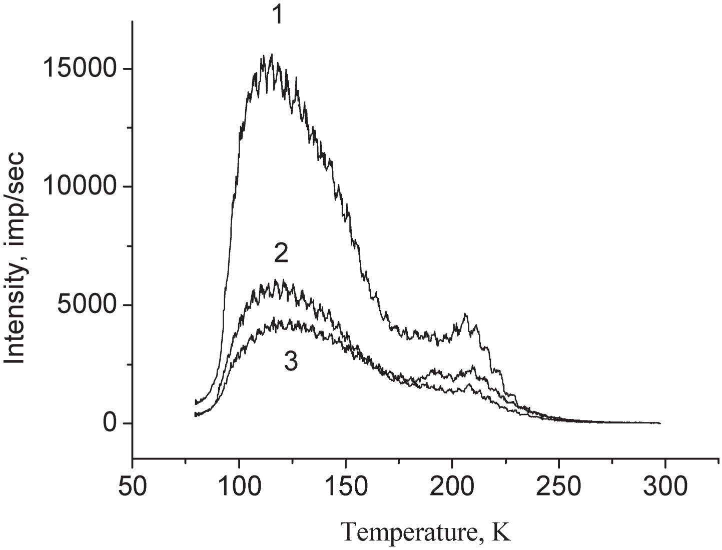

Figure 3.
Glow curves from the quenched PE-I (1) and slowly crystallized PE-II (2,3) films activated in a frozen state (−196 °C) by Ar plasma at a pressure of 13.33Pa during 1(1,2) and 0.1 s (3). Heating rate is 10 K/min.

symmetry of thermoluminescence peaks [9,10]. In the case of linear kinetics (i.e. when the probability of electron re-trapping is much lower than that of the electron-ion recombinations), a low-temperature part of a glow peak is larger than that of a high-temperature one. When the re-trapping is mostly probable (a quadratic kinetics), then a high-temperature part of a peak is more extended. As known, at low radiation dose / dose rate (similar to which we used in the experiments), a linear kinetics takes place [3]. So that in the fitting procedure we used asymmetrical double sigmoidal function extending to a low temperature side. The glow curves for both PE-I (Fig. 4) and PE-II (Fig. 5) appeared to be well fitted by 4 peaks.

It is in common practice to designate relaxation transitions by Greek letters beginning from those observed at the highest temperature. So then we designated the fitted peaks in the same manner: as α, β, γ. But the low-temperature fitted peak (at 109 K) we designated as δ′-peak in order to avoid confusing with low-temperature δ-relaxation observed in dynamic mechanical measurements in the temperature range from 20 to 70K[11]. This is assigned to the small-angle torsion vibrations of some molecular units close in size to a repeat unit of macromolecules.

The temperature positions of fitted peaks for PE-I and PE-II samples are given in Table 1 (two columns from the left side). The content of the other columns will be discussed later on.

The decomposing of the glow curves into 4 peaks implies the existence of 4 different relaxation processes activated upon heating in the investigated temperature range.

The question arises as to which relaxation processes are they attributed and mobility of which kinetic units provides trap depletion?

The relaxation processes in PE were intensively studied by many different techniques (including radiothermoluminescence) distinguishing themselves in sensitivity and detecting then the different number of relaxation transitions. The number of observable transitions depends also on PE morphology, branching of PE molecule (if any) and the experimental conditions (heating rate, frequency range…etc).

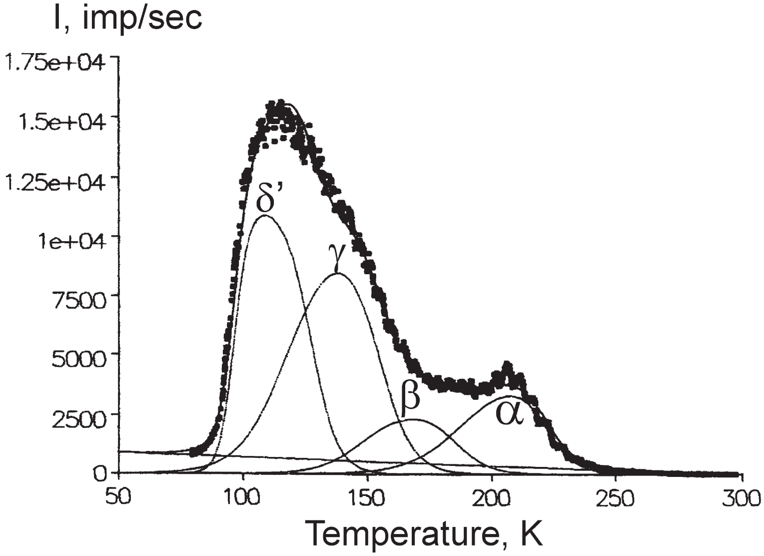

Figure 4.
Decomposition of a glow curve of PE-I film (curve 1 in Fig. 3).

All of that introduce a lot of confusion in the classification of relaxation transitions and their interpretation. This situation is well described in a number of books [2,12–14]. In general, three regions of relaxation, or unfreezing of mobility in PE are usually observed: relaxation I (at 140-170K), relaxation II (at 220–270K) and relaxation III (at

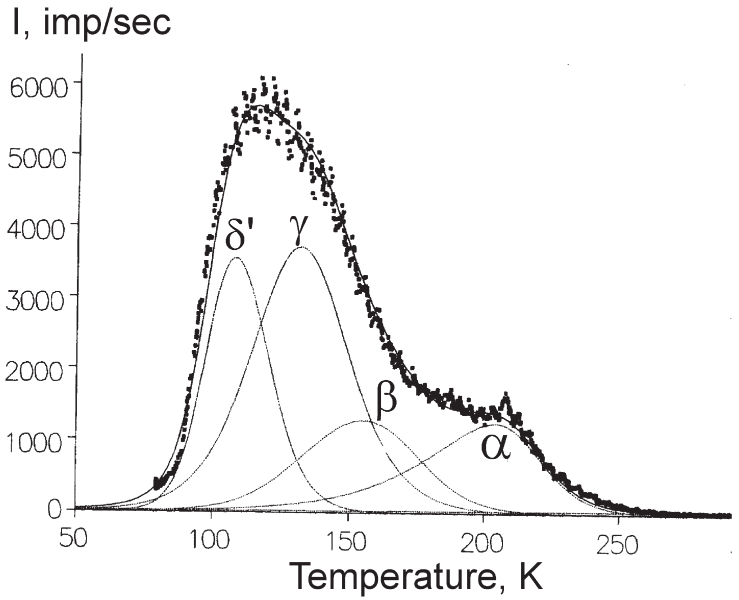

Figure 5.
Decomposition of glow curve of PE-II film (curve 2 in Fig. 3).

Table 1.
The thermal position of relaxation transitions, characteristic temperatures of the fundamental vibration and IR-active modes in a low-frequency region.

Temperature positions of glow curve fitted peaks, T, K		Relaxation regions as revealed by DSC for PE samples T, K	Characteristic temperatures of defreezing vibrations (Boltzman statistics) T, K	Maximum frequencies of fundamental vibration γ, cm^{-1}	Frequencies of IR-active modes, γ, cm^{-1}	
PE-I	PE-II					
109	109(δ')	140–170(relaxation I)	90–100	190–200	186	TT(w)
138	132(γ)			340	194	T(tw)
168	154(β)		170		311	GTT(w)
					335	TGT(w)
					336	TG(w)
207	213(α)	220–270(relaxation II)	240–290	500–600	478	GTT(w)
					456	TTT(w)

300–370K). Two of them are indicated in Table I for comparison with thermoluminescence data.

The interpretation of these transitions is, however, highly ambiguous, as regard to the kinetic units of motion involved in the relaxation transitions, in particular. The transitions at 140–170 K has most frequently been related to a local rotation event within about two monomer units in the vicinity of the defects in crystallites, on the crystallite surface or in amorphous regions. For relaxation II, the kinetic unit is regarded as a motion of the large segments, like dozens of monomer units [13,15–17].

In our case with the help of Nanoluminograph, a fine structure of relaxation I appeared to be possible to reveal in the investigated HDPE samples. Three different relaxation transitions (at $T = 109$ K, $T = 132–138$ K and $T = 154–168$ K) could be selected.

The transition at $T = 207–213$ K, should be, obviously, attributed to the relaxation II, though its temperature is lower than 220 K.

In the bulk melt-crystallized PE, four relaxation transitions can also be sometimes resolved in this temperature range. For instance, the relaxation transitions in the temperature ranges 121–125K, 194–251 K, 231–233 K and 240–236 K were observed with the help of mechanical spectroscopy [14]. Using a radiothermoluminescence technique the relaxation transitions in HDPE samples were studied, and the peaks on glow curves at 125 K, 151 K, 171 K and 223 K [18] were revealed. The samples investigated were very similar to those we studied with the help of Nanoluminograph. They had close M_w –values and were prepared in the similar conditions (quenched from the melt at a cooling rate of 30–50 degree/s). One should emphasize that the radiothermoluminescence technique, for the sample activation, applies γ-quanta having a high penetrating power. It distinguishes this technique from our experimental method. The former gives information about relaxation processes in the bulk while the latter enables one to analyze properties of the surface. It is worthy to note that the temperatures of all transitions revealed by Nanoluminograph ("surface DSC") are lower than those obtained for the bulk samples, which evidences a significant difference between surface and bulk behaviour. As known, the surface and bulk characteristics are always different at least because that the atoms on the surface have no neighbours from the side contacting to the air (coordination number is not equal to 4). It is also known that all impurities and defects upon crystallization are usually pushed out from the volume to a surface. The samples under investigations have lamellar structure.

The structure of disordered interlamellar regions in the similar HDPE sample was investigated by some of the authors of this paper with the help of X-ray analysis and NMR wide line technique [19]. At the same time the features of the molecular motion in these regions was studied using DSC [20]. It was shown that the disordered interlamellar regions depending on crystallization conditions may contain from 20 to 50% of the regular folds and from 20 to 60% of tie molecules with the different degree of coiling. Degree of coiling is $y = l/h$, where h is a distance between the ends of these molecular segments and l is their contour length. The scheme of the structure of interlamellar regions is shown in Fig. 6.

On the base of the combined analysis of DSC and NMR data, the comparison of activation barriers of motion Q(T) and "defreezing" heat of mobility of kinetic units ε (T), as well as structural data, a conclusion was drawn that the contribution of intracrystalline motion to a change in configuration heat capacity is negligible. The relaxation transitions in 150–170K and 240–270 K ranges were attributed to quasi-independent and cooperative motion of separate portions of neighbour chains, comparable to the Kuhn segment, i.e. to β- and α-relaxation in the disordered interlamellar regions. Taking into account the above conclusion, one can suggest that the observed glow-curve peaks at 207 K and 213 K be caused by the destruction of the traps at the expense of α-transition in the investigated HDPE samples. The luminescence in the 154–168 K range is associated with β-relaxation, and in 132-138 K range with γ-relaxation. The temperature position of δ'- peak does not depend on the sample preparation conditions, while the temperature of the other relaxation transitions do change for PE-I and PE-II samples. The distinction in the peak positions in quenched and slow crystallized samples is caused, obviously, by difference in conformational composition of interlamellar spaces in the surface layers. In the PE-I samples, the γ and β relaxation processes occur at slightly higher temperatures. It can be probably attributed to the possible residual stress in the quenched films. At the same time in the slowly crystallized PE-II films α-transition occurs at higher temperature. This may be associated with the enhanced content of tie molecules with lower degree of coiling as compared with that in PE-I films.

V.I.Vettegren *et al.*[21] studying relaxation in highly oriented polymers paid an attention to the coincidence of relaxation transition temperatures and the characteristic temperatures of fundamental vibrations T_{char}. [22]. At these temperatures the transition from the Bose to the Boltzmann

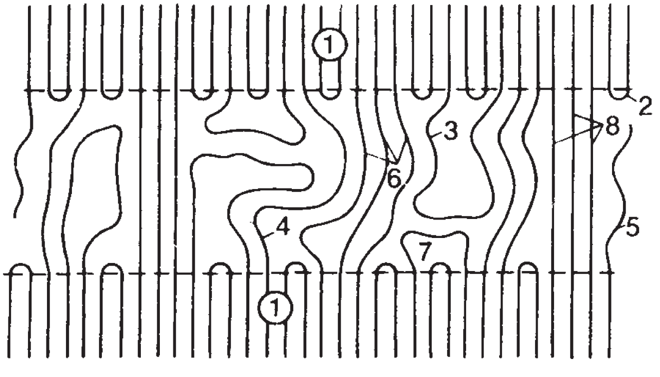

Figure 6.
Conformations in a space between lamellar crystals (1): a regular fold (2), a loose loop (3), a tie molecule with a high degree of coiling (4), cilia (5), tie molecules with a low degree of coiling (6), a fold with motion restricted by a crystal (7), taut tie molecules (8).

statistics takes place for some modes of fundamental vibrations. They assumed that an increase of the heat capacity due to a change in the statistics of the fundamental vibrations (at $T_{char} = T_{relaxation}$) allows one to generate the thermal fluctuations which play a role of a "trigger" providing a relaxation transition.

Characteristic temperatures of the defreezing of the fundamental vibrations and corresponded maximum frequencies are given in Table 1.

In our case, the structural traps, as follows from the study cited above, are located in the disordered regions. The concentration of the traps in the crystallites is negligible. It was theoretically shown [23] that there is a whole number of irregular conformers such as GTT, TGT a o. They can absorb the energy at the same low-frequency range (see Table 1). The irregular conformers may be located in the segments of molecular loose loops, or non-taut tie molecules with various degree of coiling in disordered interlamellar space. So that the energy of the defreezed fundamental vibrations at T_{char} may be transferred to the fluctuations localized on these irregular conformers in the interlamellar space (mostly wagging vibration of CH_2-groups), which will destroy the traps in the immediate vicinity of them.

The analysis of glow curve peak profiles enables one to estimate the number of CH_2-groups, comprising the kinetic units of motion in the separate relaxation transitions. Aiming at that, we calculated activation energies Q of relaxation transition using the expression

$$Q = kT_m^2/(T'' - T_m),$$

where k is the Boltzmann constant, T_m is the temperature of glow peak maximum, T'' is the temperature on the half width of glow peak on the high-temperature side.

The calculated values of $Q_{\delta'}$, Q_γ, Q_β and Q_α are given in Table 2.

It was found that in polymers there is no relationship between the cohesion energy Ec (the energy of intermolecular interaction) related to 1 mole of monomeric units and activation energy Q_β. However it was assumed [12] to consider conditionally the linear polymer as comprising from quasi-molecules (statistical segments) as the kinetic units. They established the following relationship between E_c and Q_β for these kinetic units:

$$Q_\beta \approx (0.3 \pm 0.05)E_c \cdot N + B,$$

where Q_β is the activation energy expressed in kcal per 1 mole of kinetic units, N is the number of CH_2 groups in the kinetic unit, B is the barrier of internal rotation in flexible chains, equal to 0.65 kcal/mol [24].

The activation energies estimated on the base of the analysis of the peak profiles are slightly lower than those usually cited for PE [2, 3]. However, the calculated number of CH_2-groups involving in molecular motion is not inconsistent with the estimates made by the authors in [12].

Activation energies from the thermoluminescent data can be determined by the

Table 2.

The activation energies of relaxation transitions, and the estimates of the number of CH_2-groups participating in the relaxation processes.

Relaxation transition	PE-I	PE-I	PE-II	PE-II
	Qkcal/mol	Number of CH_2-groups ina kinetic unit	Q kcal/mol	Number of CH_2-groups in a kinetic unit
δ′	1.7	3–4	1.7	3–4
γ	2.0	4–5	1.7	3–4
β	2.8	7	2.0	4–5
α	4.1		8.9	

other methods, such as multi-step heating, heating the irradiated samples at a various heating rate, ...etc [2]. We are planning to carry out these experiments in the nearest future in order to estimate a possible scatter in Q-values and in kinetic unit sizes calculated by different methods.

Conclusion

Recently made device Nanoluminograph is a powerful tool for investigation of surface properties. Due to its high sensitivity, a low dose rate/low-absorbed dose for activation the samples under investigation may be used which enables one to minimize a modifying influence of radiation, and to study the properties of a native surface. With the help of the Nanoluminograph the specificity of relaxation transitions in ultra thin surface layers of slowly crystallized and quenched HDPE films were investigated. The fine structure of relaxation spectra in low-temperature range was revealed for both samples. As follows from the thermoluminescent data, the relaxation processes in the surface layers occur at lower temperatures than the relaxation processes in the bulk. The comparison of the results with the data obtained for the similar samples with the help of DSC, NMR and WAXS/SAXS techniques in the previous study, allows one to assume that the surface layers are enriched by the molecular cilia, loose loops and molecular segments with a high degree of coiling. The comparison of the of relaxation transition temperatures of PE-I and PE-II samples leads to a conclusion that there are some residual stresses in the quenched HDPE films. The slowly crystallized films contain more molecular segments with a low degree of coiling in the disordered interlamellar regions than the quenched ones. The correlation of relaxation temperatures with the characteristic temperatures of the fundamental vibrations enabled one to assume that the trap destruction is controlled by the thermal fluctuations localizing on the irregular conformers in the disordered regions which absorb the energy transferring from the defreezed lattice vibrations.

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[1] A. A. Kalachev, N. M. Blashenkov, Yu. P. Ivanov, A. L. Myasnikov, L. P. Myasnikova, V.L. Koval' skii, Russian Federation Patent 2212650, 2003.

[2] I.V. Kuleshov, V. G. Nikol'skii, "*Radiothermoluminescence of Polymers*", chapter 3, Khimiya, Moskwa **1991**.

[3] L. Zlatkevich, "*Radiothermoluminescence and Transitions in Polymers*", chapter 3,4, Springer Verlag, New York, **1987**.

[4] V.N. Vasilez, L.A. Tikhomirov, A.N. Ponomarev, *Chem. High Energies* **1979**, *13*, 171.

[5] V.N. Vasilez, L.A. Tikhomirov, A.N. Ponomarev, *Chem. High Energies* **1981**, *15*, 77.

[6] A.A. Kalachev, T.A. Klyushina, A.M. Shapiro, V.L. Kofman, S.D. Artamonova, N.A. Plate.*Vysokomol.soed.* **1987**, *29A*, 179.

[7] A.N. Ponomarev, V.N. Vasilez, R.V. Tal'roze, *Chem.-Phys.* **2002**, *21*, 95.

[8] "*New methods of polymer investigations*", Eds. Yu.S. Lipatov, Naukova Dumka, Kiev, **1975**.

[9] V.V. Serdyuk, Yu.F. Vaksman, "*Lumin escence of semiconductors*", Vysshaya shkola, Odessa, **1988**.

[10] Ch.B. Lutschik, *Doklady Academii Nauk SSSR* **1955**, *10*, 641.

[11] V.A. Berstein, V.A. Ryzhov, in: "*Far Infrared Spectroscopy of Polym*", *Advances in Polymer Sciences, vol.114, p 43*, Eds., A. Abe, H. Benoit, HJ Cantov et al. Springer-Verlag, Berlin, Heidelberg, New York, **1994**.

[12] V.A. Berstein, E.M. Egorov, "Differential scanning calorimetry of polymers", ch.2, 3, Ellis Horwood, New York, Londom, Toronto, Sydney, Tokyo, Singapore, **1994**.

[13] "*Transitions and Relaxations in Polymers*", Ed. by R.F Boyer, Am.Chem.Soc.Symp.Held in Atlantic City, New Jersey, September 13-14, 1965: Interscience Publishers, a Division of John Wiley&Sons, Inc. 1966, J.Polym.Sci.,Part C, 14, **1966**.

[14] G.M. Bartenev, A.G. Barteneva "Relaxazionnye svoistva polimerov", ch.7, Khimiya, Moskwa **1992**.

[15] R.F. Boyer, *Polymer Sci. Polymer Symp.* **1975**, *50*, 18.

[16] R.F. Boyer, *Polymer*, **1976**, *17*, 996.

[17] Yu.M. Boiko, M.Ya. Sherman, *Polymer Science*, **1998** *40A*, 279.

[18] L.A. Osinzeva, L.Yu. Zlatkevich, M.B. Konstantinopol'skaya, V.G. Nikol'skii, V.A. Sokol'skii, A.V. Kryukov, *Vysokomol.soed*. **1974**, *16A*, 340.
[19] E.A. Egorov, V.V. Zhizhenkov, V.A. Marikhin, L.P. Myasnikova, A.A. Popov, *Vysokomol.soed*, **1983**, *25A*, 693.
[20] V.A. Berstein, V.M. Egorov, V.A. Marikhin, L.P. Myasnikova, *Vysokomol. Soed*. **1985** *27*, 1228.
[21] V.I. Vettegren, V.I. Bronnikov, S.Ya. Frenkel, in Adv.in Polym.Sci., 125, 105, Springer Verlag, Berlin Heidelberg, **1996**.
[22] G.L. Safford, A.W. Naumann, *Adv.Polym.Sci*. **1967**, *5*, 1.
[23] R.G. Snyder, *J.Chem.Phys*. **1967**, *47*, 1316.
[24] J. O'Railly, *J.App.Phys*., **1977**, *48*, 4043.