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Alterations of molecular characteristics of polyethylene under the influence of UV-radiation

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Abstract

The influence of UV-radiation on the molecular characteristics of low-density polyethylene in dependence of samples' thickness and the dose has been investigated by methods of viscosimetry, light scattering, turbidimetry and gelation measuring. It was established that the destruction and crosslinking processes of macromolecules proceed simultaneously with the irradiation. In a range of doses previous to gelation increase of mass-average molecular mass and degree of branching of macromolecules accompany the irradiation. The intensity of change of the molecular characteristics is lowered along with the increase of samples' thickness, as soon as the basic molecular transformations occur in a thin film layer of the samples' surface.

For the same reason the gelation point dose decreases along with the decrease of samples' thickness and the destruction-to-crosslinking speeds ratio rises up to a constant value, but lowers with decrease of samples' thickness.

It has been assumed that the degree of change of molecular characteristics is independent of samples' thickness and mechanisms of influence of UV- and γ-irradiation on polyethylene is similar. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Polyethylene; Radiation; Destruction

1. Introduction

In previous works the results of investigations of influence of a γ-irradiation on the molecular characteristics of low-density polyethylene (LDPE) were given depending on the samples' thickness, the intensity and dose [1,2]. A remarkable growth of average molecular mass of LDPE was established. The growth was linear for the mass-average molecular mass and at the initial doses is mainly the result of the increase of macromolecular branching. Consequently, the macromolecular effective hydrodynamic volumes have been changed and therefore the dependence of the viscosity-average molecular mass on the doses was going through minimum at the initial dose [1]. In addition, it was shown that the destruction and crosslinking processes of macromolecules proceed simultaneously with the irradiation. A significant dependence of the specified changes on irradiation intensity and irradiated samples' thickness has been established [2].

The present work will describe the results of viscosimetric, light scattering, turbidimetric and solubility investigations and the influence of ultraviolet (UV) irradiation on the LDPE in dependence of irradiation dose and samples' thickness.

It is known, that under the influence of UV-irradiation the destruction and crosslinking processes of macromolecules proceed in polymers and also the oxidizing processes are activated, especially when the irradiation is carried out in the presence of air [3–7]. It is well known that photochemical changes proceed most intensively in a surface layer of polymers, as soon as the changes fade in the process of the motion of radiation into the polymer [8–11]. The speed of oxygen absorption by the given quantity of polymer is proportional to the surface area [12] and consequently decreases with increase of polymer samples' thickness [13]. The equations describing the influence of oxygen diffusion speed of photo-oxidation of polyethylene are received [14]. The space–time evolution of the photoageing process accompanied by an increase of absorption has been studied as well. For some most important cases the formation of a limit layer was shown with the absorption profile being constant under further light action [15–16]. For the simplest cases, the evolution of the aged layer is the process of the motion of this profile into the polymer sample. The thickness of the aged layer is estimated to be 4×10^{-3} cm [17]. In the case of very thin samples, the thickness obviously does not influence the speed of oxidation any more.

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Table 1
Intrinsic viscosity's experimental ($[\eta]_g$) and calculated ($[\eta]_l$) values, mass-average molecular mass ($\bar{M}_w$), mean-square radii of gyration ($(\overline{R^2})^{1/2}$), branching index (g) and mass-average number of branching per molecule ($\bar{m}_w$) of UV-irradiated LDPE 1000, 500, 200, 100 μm. thick samples for various exposure time

Exposure (Minutes)	$[\eta]_g$ (dl g^{-1})	$[\eta]_l$ (dl g^{-1})	$\bar{M}_w \times 10^{-5}$	$(\overline{R^2})^{1/2}$ (Å)	g	$\bar{m}_w$
Samples thickness—1000 μm						
0	1.33	3.260	2.84	338	0.408	10.3
20	1.33	3.535	3.20	367	0.376	12.2
40	1.34	3.755	3.50	379	0.357	13.5
60	1.35	3.962	3.80	396	0.360	13.2
90	1.35	4.164	4.08	413	0.324	16.1
120	1.36	4.456	4.51	431	0.303	18.2
Samples thickness—500 μm						
0	1.34	3.260	2.84	338	0.411	10.2
20	1.36	3.535	3.20	368	0.384	11.7
40	1.35	3.835	3.61	379	0.357	13.5
60	1.37	4.054	3.92	396	0.337	15.0
90	1.39	4.206	4.14	413	0.330	15.6
120	1.41	4.629	4.77	431	0.305	18.0
Samples thickness—200 μm						
0	1.33	3.261	2.84	338	0.408	10.3
30	1.35	3.741	3.48	373	0.361	13.2
60	1.42	4.109	4.00	402	0.345	14.4
90	1.44	4.456	4.51	419	0.323	16.2
150	1.45	4.924	5.23	460	0.294	19.2
180	1.47	5.306	5.84	483	0.277	21.3
Samples thickness—100 μm						
0	1.34	3.258	2.84	338	0.411	10.3
30	1.40	3.681	3.40	368	0.381	12.1
60	1.42	3.998	3.84	397	0.355	13.4
90	1.45	4.316	4.30	414	0.335	15.7
150	1.48	4.843	5.10	452	0.305	18.0

Also it is shown, that the speed of crosslinking of LDPE grows by the decrease of samples' thickness and degree of crystallinity of polymers. The crosslinking occurs mainly in the amorphous phase of polymers. The increase of the degree of branching of macromolecules has a remarkable influence on the character of oxidation of LDPE [18–19].

2. Experimental

Details of the sample preparation are presented in Ref. [1]. LDPE 40, 100, 200, 500 and 1000 μm thick films have been studied.

UV-irradiation is carried out in the open air with the use of a mercury-discharge lamp with $\lambda = 253.7$ nm. The exposure intensity in the ultraviolet part of spectrum is 7 mW/cm^2. The distance from the center of the lamp to the sample is 30 cm and the temperature on the surface of the sample is about 40°C.

The viscosimetric, light scattering and turbidimetric investigations of all the samples were conducted in the range of doses in which they are practically completely soluble. Conclusions about full solubility was based on the absence of the insoluble portion after filtration of solutions through glass filter No.3.

Intrinsic viscosity measurements in Ostwald's capillary viscometer (capillary's diameter—0.64 mm) were performed in cis decalin at $70 + 0.01$°C. The efflux time of the solvent was 98 s. The solvent and solutions were filtered through a No.3 glass filter (at 70°C) before the measurements. The following formula was used for the relation of molecular mass and intrinsic viscosity [1]

$$[\eta] = 6.8 \times 10^{-4} M^{0.675}$$

The intrinsic viscosities of branched polymers ($[\eta]_g$) were measured experimentally. The intrinsic viscosity that corresponds to the linear macromolecules with the same molecular mass ($[\eta]_l$), the branching index (g, a ratio of mean-square radii of gyration of branched and linear polymer samples with the same molecular mass) and the mass-average number of branching per molecule ($\bar{m}_w$) were calculated by the ways described in Ref. [1].

The experimental errors were within allowed limits of appropriate methods and did not exceed 1% at viscosimetric and 8% at light scattering measurements. The gel contents in irradiated films were evaluated after a prolonged extraction of 2.5 g samples with hot xylene. Results were reproducible to within approximately 0.01 g.

3. Results and discussion

The values of experimental $[\eta]_g$, $\bar{M}_w$, $(\overline{R^2})^{1/2}$ and

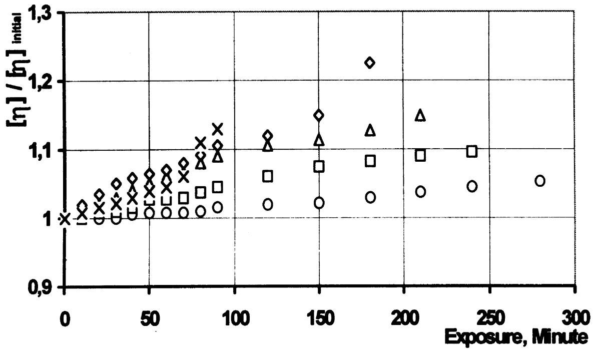

Fig. 1. The dependence of the ratio $[\eta]_g/[\eta]_{g,\mathrm{initial}}$ LDPE samples of identical thickness as a function of exposure for sample thickness (μm): circle 1000, square 500, triangle 200, rhomb 100, cross 40.

calculated $[\eta]_g$, $\bar{m}_w$ for the investigated doses and samples thickness are given in the Table 1.

The dependence of the ratio of intrinsic viscosities (consequently and $\bar{M}_v$) irradiated ($[\eta]_g$) and initial ($[\eta]_{g,\mathrm{initial}}$) samples of identical thickness from irradiation time are shown in Fig. 1 (more detailed data in Ref. [20]). As it is seen from the given diagram, with increase of irradiation time (dose) a small growth of this ratio is observed, especially for the thick samples. At the same time achievement of gel point after certain irradiation time (360, 310, 240, 210 and 120 min for the samples' thickness accordingly 1000, 500, 200, 100 and 40 μm) testifies, that an increase of molecular mass is taking place, owing to formation of intermolecular cross bonds. Further investigations of irradiated samples by the method of light scattering has fixed a considerable growth of mass average molecular mass ($\bar{M}_w$) during irradiation. The dependencies of the ratio of mass average molecular mass of irradiated ($\bar{M}_w$) and initial ($\bar{M}_{w,\mathrm{initial}}$) samples of identical thickness on irradiation time are shown in Fig. 2. Also $(\overline{R^2})^{1/2}$ has a similar behavior. The dependencies of the ratio of mean-square radii of gyration irradiated ($(\overline{R^2})^{1/2}$) and initial ($(\overline{R^2})^{1/2}_{\mathrm{initial}}$) samples of identical thickness plotted against irradiation time are shown in Fig. 3.

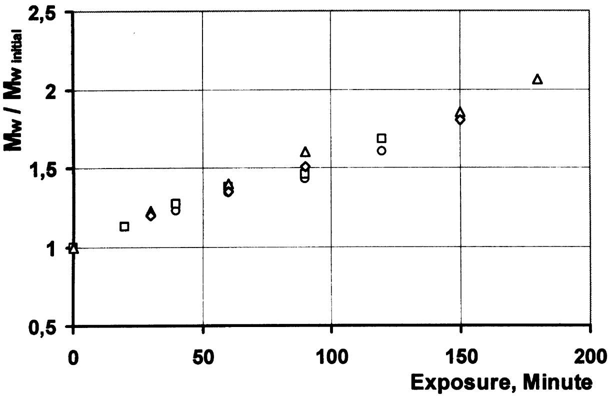

Fig. 2. The dependence of the ratio $\bar{M}_w/\bar{M}_{w,\mathrm{initial}}$ LDPE samples of identical thickness as a function of exposure for sample thickness (μm): circle 1000, square 500, triangle 200, rhomb 100.

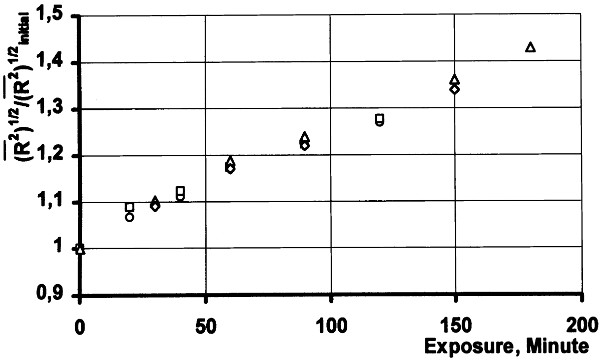

Fig. 3. The dependence of the ratio $(\overline{R^2})^{1/2}/(\overline{R^2})^{1/2}_{\mathrm{initial}}$ LDPE samples of identical thickness as a function of exposure for sample thickness (μm): circle 1000, square 500, triangle 200, rhomb 100.

These phenomena can be connected with the change of form of macromolecules during irradiation. The dependence $(\overline{R^2})^{1/2}/\bar{M}_w \sim f(\bar{M}_w)$, given in Fig. 4, can be considered as the criteria of this change. The evident decrease of $(\overline{R^2})^{1/2}/\bar{M}_w$ indicates the increase of macromolecules branching during the radiation process. However, it is considered more reliable to estimate the branching by the relation of viscosity and molecular mass, because of the difference in averaging of $\bar{M}_w$ and $(\overline{R^2})^{1/2}$ measured by the light scattering method. Thus, in Fig. 5 the relation $[\eta]_l/[\eta]_{l,\mathrm{initial}} \sim f(\bar{M}_w)$ and $[\eta]_g/[\eta]_{g,\mathrm{initial}} \sim f(\bar{M}_w)$ for different thickness of samples are shown. As it is seen from the corresponding curves, $[\eta]_l/[\eta]_{l,\mathrm{initial}} \sim f(\bar{M}_w)$ is linear and independent of the samples thickness, whereas $[\eta]_g/[\eta]_{g,\mathrm{initial}} \sim f(\bar{M}_w)$ is visibly deviating from the linearity. This fact indicates the increase of branching during the irradiation. It is evident, that the increase of molecular mass of samples occurs mainly due to the increase of branching. This conclusion is confirmed by the corresponding values of $\bar{m}_w$ (see Table 1).

Let us discuss the dependence of molecular characteristics' transformation on the samples' thickness during irradiation. A small growth of $[\eta]$ (and $\bar{M}_v$) by the decrease of samples'

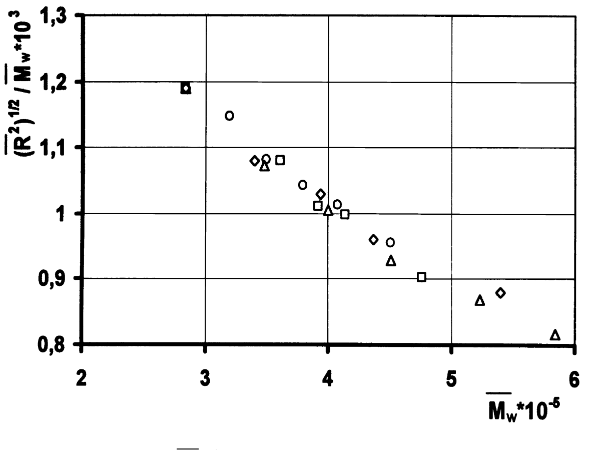

Fig. 4. LDPE samples $(\overline{R^2})^{1/2}/\bar{M}_w$ as function of $\bar{M}_w$ for the sample thickness (μm): circle 1000, square 500, triangle 200, rhomb 100.

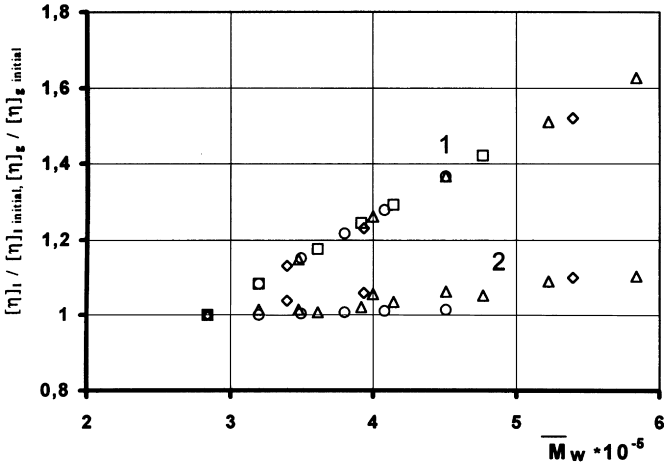

Fig. 5. LDPE samples $[\eta]_l/[\eta]_{l,\mathrm{initial}}$ (1) and $[\eta]_g/[\eta]_{g,\mathrm{initial}}$ (2) as function of $\bar{M}_w$ for the sample thickness (μm): circle 1000, square 500, triangle 200, and rhomb 100.

thickness testifies the results of Fig. 1. Also, the growth of $\bar{M}_w$ with the decrease of samples' thickness given in Fig. 2 is insignificant. The meanings of $(\overline{R^2})^{1/2}$ and $(\overline{R^2})^{1/2}/\bar{M}_w$ are independent of samples' thickness (see Figs. 3 and 4 and Table 1). Thus we conclude, that the molecular characteristics' transformation is practically independent of samples' thickness. Really, the concurrence of results of numerous investigations convinces us about the proceeding of photochemical processes on a surface layer of polymers [5–10]. The formation of a limit aged layer of a polymeric film was shown with the absorption profile being constant under further light action [15]. As already mentioned, the speed of oxygen absorption by the given quantity of polymer is proportional to the surface area [12] and consequently decreases with increase of polymer samples thickness [13]. In all results quoted in this work, we manipulate only by average values of molecular characteristics. Hence, the given quantity of polymer used for measurements contains many deep layers, not affected by irradiation at the greater thickness, which is not considered during averaging. Therefore, we consider that the observed small growth of molecular characteristics in dependence of the decrease of samples' thickness is connected by this circumstance. Further, even the probability of decreasing of molecular characteristics by decrease of samples' thickness is not excluded. Really, then we can justify the nonlinear growth of $[\eta]_g/[\eta]_{g,\mathrm{initial}}$ ratio by the doses growth for thin films given in Fig. 1, if we assume, that by thickness decreasing the degree of macromolecular branching is lowered. It can be the result of the effect of the high presence of oxygen in the photo-oxidation process for thin films. Obviously, this problem may be solved by investigations of aged surface cuts of films.

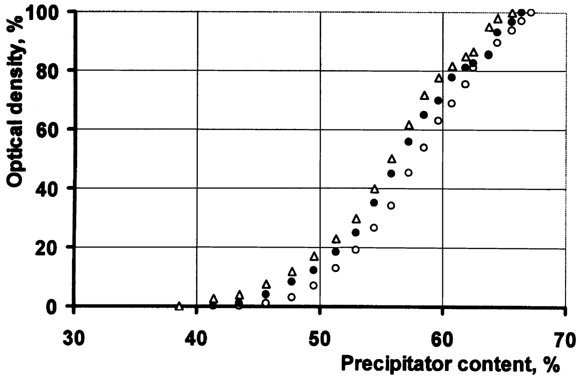

Fig. 6. The turbidimetric curves of LDPE 1000 μm thick samples for the exposures (minutes): circle 0, closed circle 40, triangle 90.

In Fig. 6 turbidimetric curves of initial and irradiated of various duration's samples are given (samples thickness—1000 μm). As it is shown, the bimodality of turbidimetric curves is observed for the irradiated samples. It shows two irradiation concomitant processes—destruction and crosslinking. With the increase of irradiation time (dose) the precipitate thresholds shifts to the left which testifies to increase of high molecular fraction in a sample. The investigation of samples of smaller thickness has given similar results. The greater expression of these processes should be noted in case of smaller thickness, taking into consideration the influence of the surface oxidation effects.

The results of definition of gel content as a function of exposure time for the different thickness films of LDPE are given in Fig. 7. The data testifies the lowering of gel point dose with the decrease of thickness (360, 310, 240 and 210 min for thicknesses of 1000, 500, 200 and 100 mm) that will be well coordinated to the behavior of change of the molecular characteristics of the same samples from the irradiation time (see Figs. 1 and 2). The trend in the data specifies, that for all thickness the relative magnitudes of chain destruction and chain crosslinking processes when both occur simultaneously to estimate the extent of crosslinking relative to destruction during the initial exposure. However, as the trend further indicates, the ratio of destruction-to-crosslinking frequency mounts to constant

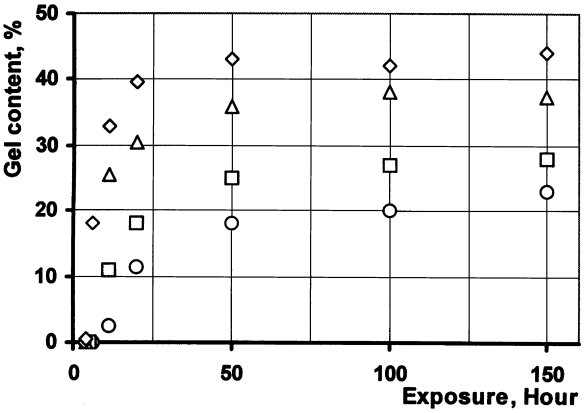

Fig. 7. LDPE samples gel fraction percentage as function of exposures (hour) for sample thickness (μm): circle 1000, square 500, triangle 200, rhomb 100.

values. It might be caused by a highly crosslinked rigid structure inhibiting further crosslinking reaction. The comparison of rates of gel formation during irradiation for different thickness films shows that the chain destruction is favored in thicker films. Obviously it can be connected to the fact, that the basic radiative chemical processes of UV-irradiation are located in surface limited layer of polymer film [15].

4. Conclusion

The viscosimetry, light scattering, turbidimetry and gelation measuring investigations of ultraviolet irradiated LDPE in open air testify that the chain destruction and crosslinking processes take place simultaneously. Consequently, the correlations of molecular fractions of LDPE are changed. At the initial exposure of radiation, the crosslinking process is prevailing. But in further irradiation the ratio of destruction-to-crosslinking frequencies is increasing to constant values obviously because of forming highly crosslinked rigid structure inhibiting further crosslinking reaction.

It was obtained, that for the given samples' thickness by the irradiation exposures growth the speed of mass-average molecular mass is higher than that for intrinsic viscosities values. The phenomena are explained by the growth of degrees of macromolecules chain branching.

Also, it was obtained, that the molecular characteristics' transformation practically is independent of samples' thickness. Even the probability of decreasing of molecular characteristics by samples' thickness lowering was not excluded. This fact and the fact, that the gel content percentage is lowered by the samples' thickness growth, is argued by the circumstance, that the basic radiative chemical processes of UV-irradiation are located in surface limited layers of polymer films.

The qualitative comparison of the results of the influence of γ- and UV-radiation on LDPE indicate, that both destruction and crosslinking processes occur simultaneously in both forms of influence. The influence is limited only by diffusion of oxygen during γ-irradiation, when it is limited both by diffusion of oxygen and penetration of radiation during UV-irradiation. Consequently the molecular transmissions are deeper and evident in case of γ-irradiation, as soon as the polymer is transformed in whole volume, whereas the molecular transmissions in case of UV-irradiation are proceeding in the layer surface area.

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