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Effect of γ-radiation on the molecular characteristics of low-density polyethylene

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Abstract

The influence of γ-radiation on the molecular characteristics of low-density polyethylene dependant on the samples' thickness, the intensity and the dose has been investigated by methods of viscosimetry and light scattering. A remarkable increase of molecular mass by the increase in radiation doses was established. It is linear for the mass-average molecular mass while for the viscosity average molecular mass it is minimum at the initial doses. The origin of this minimum is explained by the change of macromolecular hydrodynamic volume, as it has also been established that the growth of molecular mass at the initial doses is mainly due to the increase of the degree of macromolecular branching. A dependence of the rate of change of polyethylene molecular characteristics on the samples' thickness, irradiation intensity and dose was established. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Polyethylene; Radiation; Macromolecular branching

1. Introduction

It is known that the noninvertible molecular transformations occur in the polymers by irradiation, resulting in a change of supermolecular structure and, accordingly, the exploitation characteristics of the amorphous-crystalline polymers [1,2]. Consequently, the elucidation of the regularities of changes in the molecular characteristics under the influence of external factors represents a considerable interest for the investigation of previously studied polymers with respect to growth and stabilization. In the present paper we report and discuss the results of viscosity and light scattering investigations of the influence of γ-radiation on molecular characteristics of low-density polyethylene (LDPE) dependent on the samples' thickness, the irradiation intensity and doses.

2. Experimental

LDPE 100, 200, 500 and 1000 μm thick films were studied. They were made by the hot-pressing method on the hydraulic press device DP-36 (DDR). Irradiation was carried out on the device RCM-20 in the open air by a standard ^{60}Co source (taking into account the disintegration of source). The irradiation intensities were 0.1 and 0.4 Mrad h^{-1} (1 Mrad $h^{-1} = 2.78$ Gy s^{-1}, 1 Gy $= 10^2$ rad). The temperature on the film surface was 40°C.

Intrinsic viscosity measurements in Ostwald's capillary viscometer (the 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. For the relation of molecular mass and intrinsic viscosity (unit of [η] dl g^{-1}) the following formula was used [3]

$$[\eta] = 6.8 \times 10^{-4} \times M^{0.675}. \quad (1)$$

Light scattering measurements were performed in *cis* decalin at 80°C on the light scattering instrument FPS-3 (constructed by the Central Constructional Bureau of Academy of Sciences, USSR) with unpolarized incident light ($\lambda = 436$ nm). Scattering intensities were measured over the angular range 30–150° with benzene as reference ($Iu = 48.5 \times 10^{-6}$ cm^{-1}). The refractive index increment ($\partial n/\partial c$) was measured on a Pulfrikh differential refractometer in *cis* decalin at 80°C by using a mercury-discharge lamp with blue light (435.8 nm), giving $\partial n/\partial c = 0.109$ cm^3 g^{-1}. In order to purify the solvent and solutions, they were successively filtered through the glass filters of different sizes (No. 3–5) thermostated at 80°C.

The mass-average molecular mass ($\bar{M}_w$) and mean-square radius of gyration $(\overline{R^2})^{1/2}$ of initial samples were determined

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Table 1
Values of experimental $[\eta]_g$, $\bar{M}_w$, $(\overline{R^2})^{1/2}$ and calculated $[\eta]_l$, g, $\bar{m}_w$ for the irradiation intensities 0.4 and 0.1 Mrad h^{-1} and samples thickness 1000, 500, 200, 100 μm

Irradiation dose (Mrad)	$[\eta]$ (dl g^{-1})		$\bar{M}_w \times 10^{-5}$		$(\overline{R^2})^{1/2}$ (A)		$[\eta]_l$ (dl g^{-1})		g		$\bar{m}_w$	
	Irradiation intensity (Mrad h^{-1})											
	0.4	0.1	0.4	0.1	0.4	0.1	0.4	0.1	0.4	0.1	0.4	0.1
Samples thickness—1000 μm												
0	1.32	1.33	2.80	2.81	338	338	3.23	3.24	0.41	0.41	10	10
0.05	1.28	1.26	3.14	2.98	362	355	3.51	3.37	0.36	0.37	13	12
0.3	1.38	1.39	3.68	3.44	391	387	3.85	3.72	0.35	0.37	13	12
0.7	1.60	1.52	4.60	4.35	449	451	4.51	4.35	0.35	0.35	14	14
0.9	1.64	1.68	5.10	4.70	487	483	4.84	4.81	0.34	0.33	15	15
1.5	1.82	1.83	6.51	5.84	555	518	5.71	5.30	0.32	0.34	17	14
Samples thickness—500 μm												
0	1.32	1.33	2.76	2.81	338	338	3.23	3.23	0.40	0.41	11	10
0.05	1.06	1.22	3.27	3.02	391	374	3.58	3.55	0.30	0.34	18	14
0.2	1.37	1.30	3.58	–	420	–	3.93	–	0.35	–	14	–
0.3	1.38	1.36	–	3.50	–	420	–	3.50	–	0.36	–	13
0.5	1.55	–	4.22	–	465	–	4.26	–	0.36	–	13	–
0.7	1.60	1.45	–	4.60	–	472	–	4.51	–	0.32	–	16
0.9	1.70	1.53	5.17	5.12	527	495	4.88	4.85	0.35	0.31	14	17
1.5	1.91	1.75	7.27	6.85	620	612	6.25	5.90	0.31	0.29	17	19
Samples thickness—200 μm												
0	1.34	–	2.76	–	338	–	3.20	–	0.42	–	10	–
0.01	1.20	–	3.22	–	397	–	3.55	–	0.34	–	14	–
0.3	1.46	–	4.00	–	424	–	4.11	–	0.35	–	14	–
0.5	1.58	–	4.62	–	478	–	4.53	–	0.34	–	14	–
0.7	1.60	–	5.18	–	506	–	4.89	–	0.33	–	15	–
0.9	1.73	–	6.10	–	535	–	5.46	–	0.32	–	17	–
1.3	1.85	–	7.55	–	620	–	6.31	–	0.29	–	19	–
Samples thickness—100 μm												
0	1.32	1.33	2.74	2.81	349	338	3.18	3.23	0.41	0.41	10	10
0.01	1.32	1.32	2.97	–	367	–	3.36	–	0.39	–	11	–
0.05	–	1.38	–	3.18	–	373	–	3.52	–	0.39	–	11
0.2	1.48	1.41	3.73	–	408	–	3.92	–	0.37	–	12	–
0.3	–	1.45	–	3.66	–	414	–	3.87	–	0.37	–	12
0.5	1.64	1.54	4.85	4.40	466	448	4.67	4.38	0.35	0.35	13	14
0.9	1.82	1.68	6.44	5.75	542	521	5.66	5.25	0.32	0.32	16	16

by both the methods of Zimm and Debye on the assumption about the shape of the macromolecules to be as Gauss coil. Similar results have been obtained. So, in a further investigation the less complex Debye method was applied.

The intrinsic viscosity of branched polymers ($[\eta]_g$) was measured by experiment. Inserting the measured values of branched polymer samples $\bar{M}_w$ into Eq. (1) the $[\eta]_l$ values were calculated, which correspond to the linear macromolecules with the same molecular mass. Then, the branching index was defined as the ratio of measured $[\eta]_g$ and calculated $[\eta]_l$. It was determined as a ratio of mean-square radii of gyration of linear and branched polymer samples with the same molecular mass.

$$\frac{[\eta]_g}{[\eta]_l} = \frac{(\overline{R^2})_g^{3/2}}{(\overline{R^2})_l^{3/2}} = g^{3/2}. \tag{2}$$

It was assumed that the Kuhn segments' length is the same for both the linear and the branched chains.

The truth of this relation is proved in Ref. [4], where the dimensions of LDPE in the same solvent were investigated.

The value of g is connected which the mass-average number of branching per molecule ($\bar{m}_w$) by the Zimm and Stockmayer theoretical relation, obtained for polydisperse, trifunctional, statistically branched chains [5].

$$g = \frac{6}{\bar{m}_w}\left[\frac{1}{2}\left(\frac{2+\bar{m}_w}{\bar{m}_w}\right)^{1/2}\ln\left(\frac{(2+\bar{m}_w)^{1/2}+\bar{m}_w^{1/2}}{(2+\bar{m}_w)^{1/2}-\bar{m}_w^{1/2}}\right)-1\right]. \tag{3}$$

Using this relation the values of $\bar{m}_w$ were calculated.

Many investigations have been devoted to the problem of long-chain branching of LDPE, assuming that the LDPE branching character is trifunctional [6–8].

3. Results and discussion

The numerous experimental results obtained by different authors testify that the main radiochemical effects in

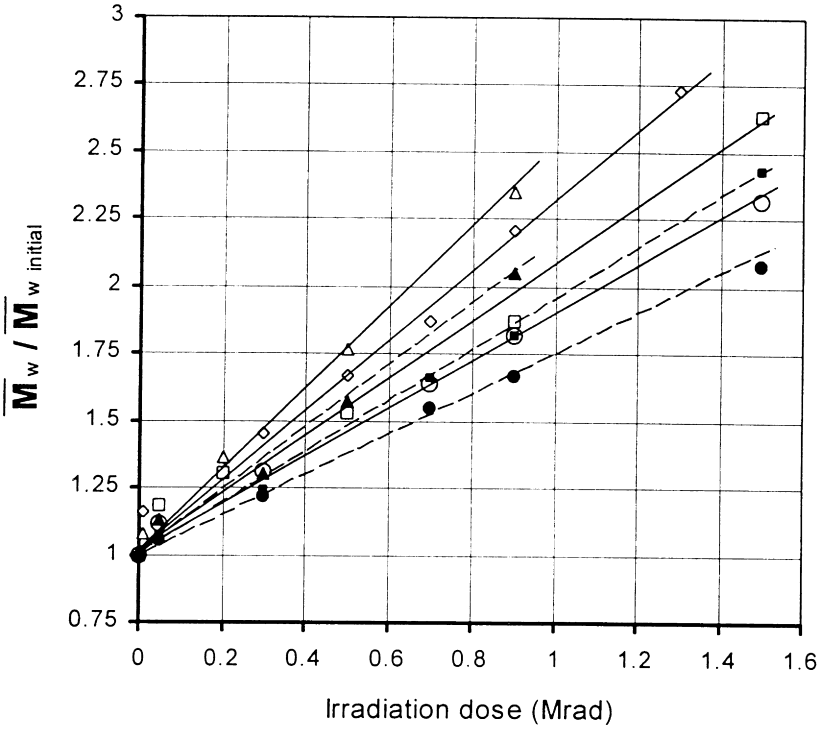

Fig. 1. The increase of LDPE samples M_w as a function of irradiation dose for sample thickness (μm): circle—1000, square—500, rhomb—200, triangle—100. Irradiation intensities: 0.4 (continuous line, open symbols) and 0.1 Mrad h^{-1} (dotted line, closed symbols).

polyethylene caused by radiation are macromolecular chain destruction, crosslinking and the emergence of double bonds [1,2]. On the occasion of irradiation of polyethylene in the open air these processes were simultaneous. Moreover, it is known that the destruction of chains is considerably intensified because of polymer oxidation.

In our work the investigations of all the samples were conducted in the range of doses in which they are practically completely soluble. Exhaustive extraction was used for the solubility investigations. *Cis* decalin is used as a solvent at 70°C. Total solubility is based on the total absence of insoluble material. The level of radiation dose, at which the sample loses its solubility, depends on the thickness. This dose increases simultaneously with the thickness.

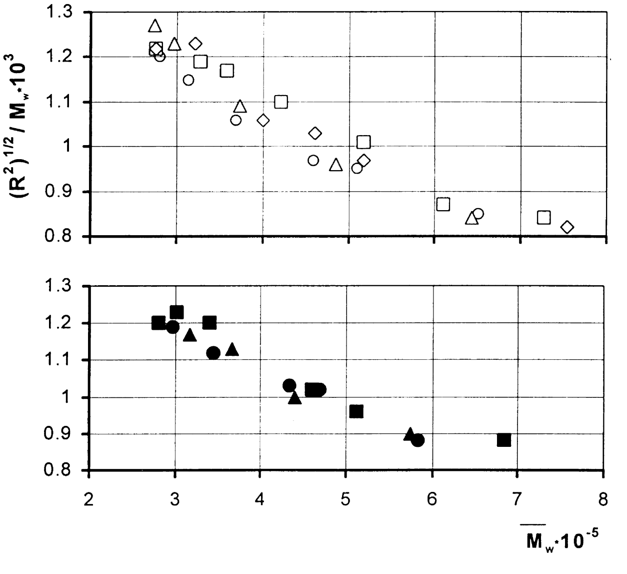

Fig. 2. LDPE samples $(\overline{R^2})^{1/2}/\bar{M}_w$ as function of $\bar{M}_w$ for the sample thickness (μm): circle—1000, square—500, rhomb—200, triangle—100. Irradiation intensities: 0.4 (open symbols) and 0.1 Mrad h^{-1} (closed symbols).

In Table 1, the values of experimental, $[\eta]_g, \bar{M}_w, (\overline{R^2})^{1/2}$ and calculated $[\eta]_l$, g, $\bar{m}_w$ for the investigated doses and samples thickness are given.

As shown in Table 1, the values of $[\eta]_g$ (consequently of $\bar{M}_v$) increase simultaneously with the increase in the dose, but they are at a minimum at the initial doses (more detailed data in Ref. [9]). Moreover, the minimum depth depends on the sample thickness and is the highest at the 500 μm thickness. It seems these phenomena can be connected with the superiority of the destruction process over the crosslinking in the initial doses. But further investigations of samples by light scattering method show that the mass-average molecular mass increases linearly along with an increase in the dose. The $(\overline{R^2})^{1/2}$ also has a similar behavior. Fig. 1 illustrates the dependence of molecular mass increase on the irradiation dose for the two intensities.

The analysis of Table 1 shows, that during all the investigated intervals in the process of destruction and crosslinking, the degree of macromolecules branching increases. The dependence $(\overline{R^2})^{1/2}/\bar{M}_w \sim f(\bar{M}_w)$, given in Fig. 2, can be considered as the criteron of this change. The evident decrease of $(\overline{R^2})^{1/2}/\bar{M}_w$ indicates the increase

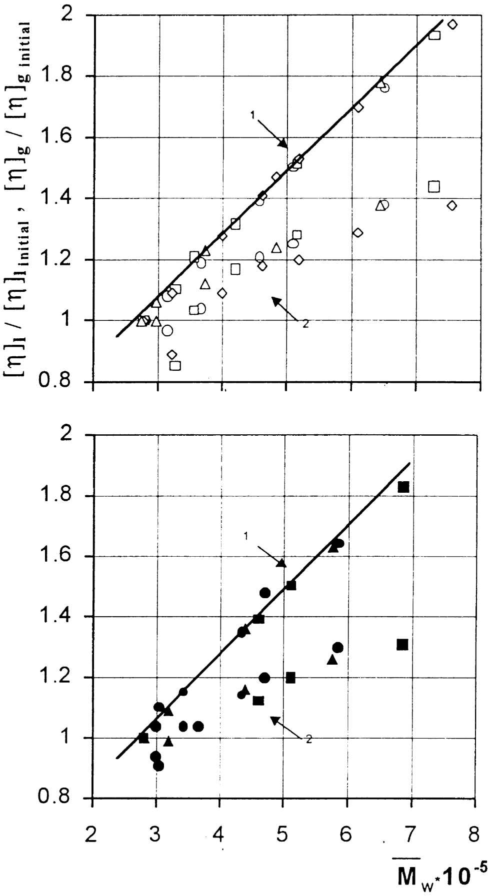

Fig. 3. LDPE samples $[\eta]_l/[\eta]_{l\ \mathrm{initial}}$ (1) and $[\eta]_g/[\eta]_{g\ \mathrm{initial}}$ (2) as function of $\bar{M}_w$ for the samples thickness (μm): circle—1000, square—500, rhomb—200, triangle—100. Irradiation intensities: 0.4 (open symbols) and 0.1 Mrad h^{-1} (closed symbols).

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 [3], because of the difference in averaging of $\bar{M}_w$ and $(\overline{R^2})^{1/2}$ measured by the light scattering method. In Fig. 3 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 thicknesses of samples and both intensities 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 sample thickness, whereas $[\eta]_g/[\eta]_{g\ \mathrm{initial}} \sim f(\bar{M}_w)$ is visibly deviating from the linearity and is at a minimum at the initial doses. This fact indicates the increase of branching during the irradiation especially at the initial doses. It is evident that at the initial doses the increase of molecular mass of a sample increases mainly due to increased branching. This conclusion is confirmed also by the different slopes of curves in Fig. 2 in the initial and further doses and by the corresponding values of $\bar{m}_w$ (see Table 1). Also, the dependence of branching on the samples' thickness can be estimated.

The dependence of the efficiency of irradiation on the samples' thickness is evident (the values of [η] and $\bar{M}_w$ in fixed doses are growing along with the decrease in the samples' thickness). This means that the velocity of the growth of molecular characteristics is dependent on the increase in dose as the sample thickness decreases. Moreover, it is clear from Figs. 1 and 2, that for films of identical thickness the velocity of a molecular characteristic's growth is less for 0.1 Mrad h^{-1} than for 0.4 Mrad h^{-1}, depending on the dose. We attribute these facts to the limitation of oxygen diffusion in the sample depth. The samples' great thickness makes it difficult for oxygen to diffuse into the polymer depth and thus they are resistant to the growth radiance.

The degree of irradiation effect depends on the intensity. As seen from Fig. 1 and Table 1, the values of [η] and $\bar{M}_w$ for 0.1 Mad h^{-1} are lower than for 0.4 Mad h^{-1} (for identical doses). It is notable that in the case of 0.1 Mrad h^{-1} the decrease in doses observed corresponds to the gel fraction appearance (for the samples of identical thickness). Obviously, all these phenomena take place due to the fact that for a lower intensity considerably longer time is required for the radiation to reach the corresponding dose.

4. Conclusions

The viscosity and light scattering investigations of γ-irradiated LDPE in open air show a linear growth of $\bar{M}_w$ and $(\overline{R^2})^{1/2}$ by the growth of radiation dose, whereas for the viscosity-average molecular mass the related curve goes through a minimum at the initial doses. Evidently, the origin of this minimum is connected with the change of macromolecular hydrodynamic volume, as the growth of molecular mass of the initial doses is mainly due to the increase in the degree of macromolecular branching.

The velocity of change of these characteristics' growth depends on the irradiation intensities and samples' thickness. It is explained by the limitation of oxygen diffusion towards the sample depth and by the prevalence of destruction processes over the crosslinking during the lingering irradiation in the presence of air oxygen until given irradiation doses are obtained.

References

[1] Charlesby A. Atomic radiation and polymers. Oxford: Pergamon, 1960 chap. 13.
[2] Dole M. In: Dole M, editor. The radiation chemistry of macromolecules, New York: Academic, 1972 chap. 14.7.
[3] Raphikov IN, Boodtov VP, Monakov UB. Introduction in a polymers physical chemistry. Moscow: Science, 1978.
[4] Shtennikova IN, Kornieva EB, Bichkova BE. Vysokomolek Soedin 1972;B14:118.
[5] Zimm BH, Stockmayer W. J Chem Phys 1949;17:1301.
[6] Bower TN. Polym Sci 1977;10:118.
[7] Culter D. J Polym Sci 1977;10:1005.
[8] Vile J, Hendra PS, Willes HA, Cudby ME. Polymer 1984;8:1173.
[9] Barkhudaryan VG, Avetisyan MG. Uch Zapisky YGU 1987;3:55.