

# Alterations of molecular characteristics of polyethylene under the influence of $\gamma$ -radiation

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## Abstract

The effect of  $\gamma$ -irradiation on the molecular mass distribution and solubility of low-density polyethylene (LDPE) in dependence of samples' thickness, irradiation intensity and dose have been investigated by the methods of turbidimetry and gelation measuring. Irradiation took place in the presence of air. It was shown that the destruction and crosslinking processes proceed simultaneously with the irradiation. The expressiveness of these processes depends on the irradiation intensity, dose and samples' thickness. Also, the decrease of gel point occurrence and difference in velocities of degradation and crosslinking of macromolecules were established along with the decrease of the samples' thickness and irradiation intensity. © 1999 Elsevier Science Ltd. All rights reserved.

*Keywords:* Polyethylene; Irradiation; Crosslinking

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## 1. Introduction

In the previous paper, the effect of  $\gamma$ -irradiation on the molecular characteristics of low-density polyethylene (LDPE) was investigated by the methods of viscosimetry and light scattering in doses prior to gelation [1]. A remarkable growth of average molecular mass of LDPE along with the irradiation dose growth 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 the macromolecular branching. As a result, the macromolecular hydrodynamic volumes have been changed, and therefore the dependence of the viscosity-average molecular mass on the doses was going through the minimum at the initial doses. Also, the dependence of the velocity of change of molecular characteristics on irradiation intensity ( $\Pi$ ) and sample thickness was established [1]. Obviously, these results are consequent to the fact that the main radiochemical effects caused by radiation to LDPE are macromolecular chain destruction and crosslinking [2]. Also, it should have effect on the LDPE macromolecular mass distribution (MMD) and solubility. The results of these investigations will be described in this paper.

There are many papers devoted to this problem [1–20], including review papers [10,11]. It is shown that the efficiency of crosslinking increases in vacuum [2] and in an

inert environment [12,13], while the radiative oxidation and subsequent destruction of macromolecules is intensified when polyethylene is irradiated in the presence of oxygen [14,15]. Moreover, during the radiative oxidation of polyethylene the double structure in the thick samples is being formed, which contains the upper oxidated and the inner crosslinked layers [16]. It was discovered that there exists a direct proportionality of the thickness of oxidated layer and the  $\Pi$  [17]. In several old investigations, the dependence of the characteristics of polymers on  $\Pi$  is denied [2,18]. However, there is evidence about its influence on the processes, which proceed in polyethylene under irradiation [11,14,17,19].

## 2. Experimental

Details of the sample preparation, irradiation procedure and intrinsic viscosity measurements are given in Ref. [1]. LDPE 1000, 500, 200 and 100  $\mu\text{m}$  thick films were studied. Irradiation was carried out in the open air by a standard  $^{60}\text{Co}$  source. The  $\Pi$ s were 0.4 and 0.1 Mrad  $\text{h}^{-1}$ .

The MMD were investigated on the photoelectrical turbidimeter device FET by mercury-discharge lamp. The thermodynamically compatible pair *cis*-decalin–isoamyl alcohol was used as a system of solvent-precipitator at the temperature 80°C. The MMD investigations of all samples were conducted in the range of doses in which they are

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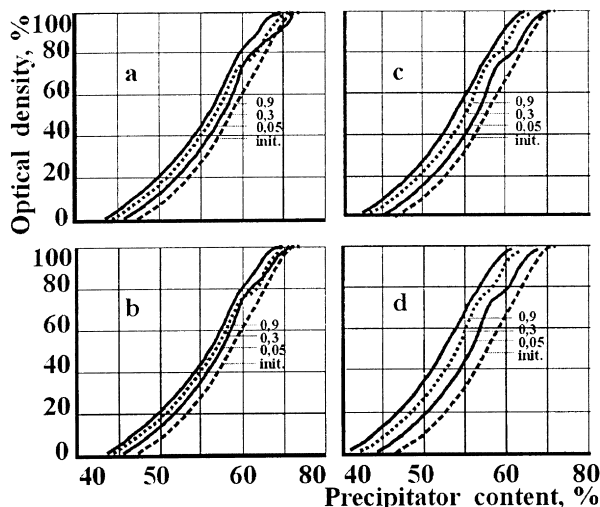


Fig. 1. The turbidimetric curves of LDPE for the samples' thickness ( $\mu\text{m}$ ): (a) 1000; (b) 500; (c) 200; (d) 100. Irradiation doses (Mrad) are given on the curves.

completely soluble. Conclusion about a full solubility was based on the absence of the insoluble portion.

As in many works [3–6] the exhaustive extraction was used for the solubility investigations. *O*-xylene is used as a solvent at  $80^\circ\text{C}$ . The quantities of crosslinked polymer (gel fraction) were obtained by the determination of the insoluble portion. It was defined as the polymer portion separated from the solution phase. The swelling time of extraction was

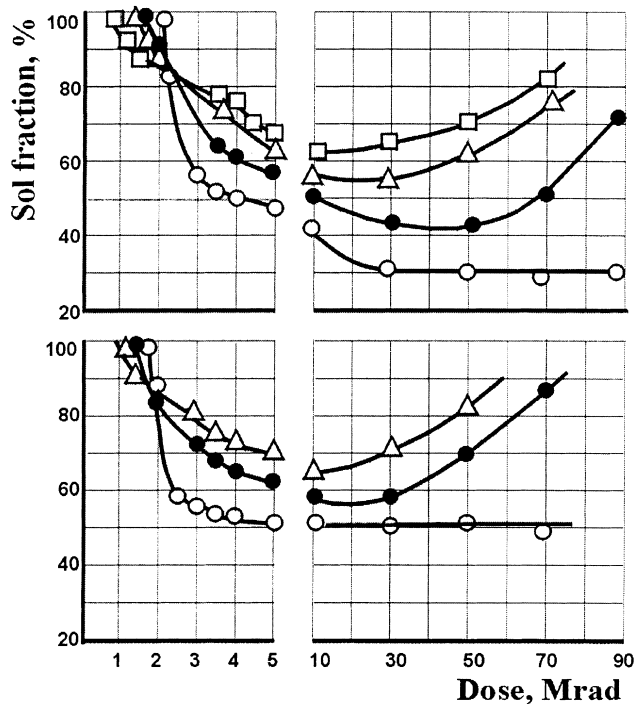


Fig. 2. LDPE samples sol fraction percentage as a function of irradiation doses (Mrad) for sample thickness ( $\mu\text{m}$ ): (○) 1000; (●) 500; (▽) 200; (□) 100. Irradiation intensities: (a) 0.4 and (b) 0.1 Mrad  $\text{h}^{-1}$ .

24 h, after which the solutions were filtered through a No. 3 glass filter at the temperature of  $80^\circ\text{C}$ . The insoluble portion was washed with hot xylene then it was removed from the gel fraction in a vacuum oven, also at the temperature of  $80^\circ\text{C}$  until the constant weight.

### 3. Results and discussion

The turbidimetric curves of different thick films of LDPE for the different irradiation doses are given in Fig. 1. The II was  $0.4 \text{ Mrad h}^{-1}$ . The results of sol fraction determination as a function of dosage for the different thick films of LDPE are given in Fig. 2. The IIs were 0.4 and  $0.1 \text{ Mrad h}^{-1}$ .

Fig. 3 illustrates the dependence of crosslinking coefficients on the dose for the two intensities. As it is known [2] it is defined as the number of crosslinked units per initial mass-average molecule.

As it is seen from Fig. 1, the bimodality of turbidimetric curves is observed starting from little doses. It testifies to the two irradiation-concomitant processes—destruction and crosslinking. The bimodality is expressed less evidently for the greater doses of irradiation, since obviously the crosslinking process is prevailing before the gel point occurs. Due to the high molecular fraction growth in the samples, the precipitate thresholds shift to the left with the increase of dose. They shift to the left also with the decrease of the samples' thickness for the given dose. These results correspond to the earlier obtained data regarding the growth of average molecular mass with the decrease of samples' thickness for the given dose [1].

Herewith we present the results for II at  $0.4 \text{ Mrad h}^{-1}$  since the obtained phenomena were similar for II at  $0.1 \text{ Mrad h}^{-1}$ . A greater expression of these processes should be noted in the case of smaller II, taking into consideration the influence of the surface-oxidation time effects.

Let us discuss the data in Fig. 2. They testify the gelation point dose growth with the growth of the samples' thickness. This result also corresponds to the linear growth of mass-average molecular mass with the decrease of the samples' thickness for the given dose [1]. The gelation point doses of the samples, with the same thickness, shifts to the left in case of lower II. It is natural, since for lower intensity considerably longer time is required to reach the given dose, so the molecular transmissions of macromolecules are proceeding at a longer time.

Also, the velocities of destruction and crosslinking processes distinctly depend on the samples' thickness, II and dose. It is not possible to determine quantitative values of the destruction-to-crosslinking probabilities ratio ( $p_0/q_0$ ) by the method of Charlesby and Pinner [2] for this polymer especially when it was irradiated in the open air, since the data do not show a linear relation between  $S + \sqrt{S}$  and  $1/r$ , where  $S$  is the sol content and  $r$  is the dose of irradiation. However, the trend in the data would clearly indicate to the changing  $p_0/q_0$  ratio with the growth of the irradiation

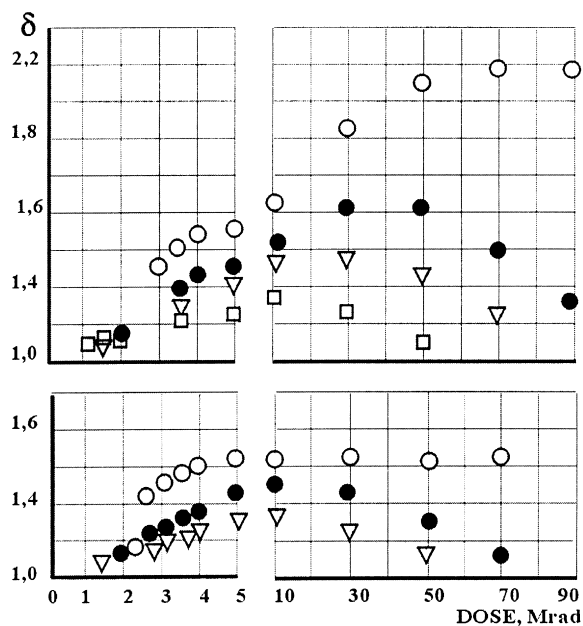


Fig. 3. Number of crosslinked units per molecule as a function of irradiation doses (Mrad) for sample thickness ( $\mu\text{m}$ ): (○) 1000; (●) 500; (▽) 200; (□) 100. Irradiation intensities: (a) 0.4 and (b) 0.1  $\text{Mrad h}^{-1}$ .

doses. Also, the same behavior have the number crosslinked units per molecule ( $\delta$ ) given in Fig. 3 which were determined by the relation  $S + \sqrt{S} = 2/\delta$  [2]. They increased to maximum values with the growth of the radiation doses and did give conclusive evidence of different destruction-to-crosslinking ratios for different thick samples. Then they evidently decreased because the destruction processes prevailed. It seems quite appropriate, since the oxidation processes take place in the thin film layer of the samples' surface when it is irradiated in the presence of air oxygen [14–17].

Generally, the degree of gelation grows with the growth of the doses for all thick samples. However, for the given dose the percentage of gelation decreases along with the decrease of the samples' thickness and II. It allows us to

Table 1  
Values of sol fractions  $[\eta]$  ( $\text{dl g}^{-1}$ ) for II 0.4 and 0.1 ( $\text{Mrad h}^{-1}$ ) and the samples' thickness 1000, 500, 200, 100 ( $\mu\text{m}$ )

Irradiation dose (Mrad)	Samples' thickness ( $\mu\text{m}$ )			
	1000	500	200	100
<i>Irradiation intensity 0.4 Mrad h<sup>-1</sup></i>				
10	1.71	1.58	1.34	1.20
20	1.52	1.32	1.21	1.08
30	1.43	1.18	0.92	0.76
<i>Irradiation intensity 0.1 Mrad h<sup>-1</sup></i>				
10	1.64	1.35	1.16	1.04
20	1.45	1.16	1.05	0.72
30	1.36	0.92	0.78	0.41

suppose that the destruction processes occur primarily in the surface area of the samples in the presence of diffused oxygen. By the same reason, the samples' thickness considerably influence the polymers' full degradation dose (70, 90 and 120 Mrad for the sample thicknesses of 100, 200 and 500  $\mu\text{m}$ , respectively). The full degradation of samples is based on the absence of intrinsic viscosity of their solutions. (The efflux time of solvent and solution were identical.)

Also, by the method of viscosimetry the intensification of degradation process of macromolecules are fixed by the increase of irradiation dose and decrease of samples' thickness, and II. In Table 1 are given the results of sol fraction intrinsic viscosity measurements in dependence of samples' thickness, II and dose (performed in xylene at 80°C). As it is seen from the table, with the increase of dose, there is observed a remarkable decrease of  $[\eta]$  (consequently of  $\bar{M}_v$ ) with the velocity depending on samples' thickness and II. These facts once more indicate that the destruction process of macromolecules in the surface area occurs as general.

One of the most interesting results is the presence of isogelation point (the value of dose in which all the thick samples have the same gel content) on the curves, representing the relation of the percentage of sol fraction versus the doses. This point shifts to the left at the lower intensity. Obviously, it is simply a result of surface effects, but we are not able to explain this fact more effectively.

#### 4. Conclusions

The turbidimetric investigations of LDPE testify that the destruction and crosslinking processes take place simultaneously when it is irradiated in the presence of air oxygen. As a result, the correlations of molecular fractions are changed. The expressiveness of these processes becomes evident with the decrease of samples' thickness.

The gelation measuring of irradiated LDPE shows the generation of gel fraction. The velocity of crosslinking is prevailing at the initial doses. However, the destruction-to-crosslinking velocities ratio increases with the growth of the irradiation doses. This ratio increases also with the decrease of samples' thickness and II. These facts indicate that the destruction of macromolecules occur primarily in the surface area of the polymer in the presence of diffused oxygen.

The work shows quite clearly that the presence of oxygen plays an important role in the effect of ionizing radiation on LDPE, it seems obvious that the effect of II and samples' thickness is equally important.

It must be noted that the problem of importance of II for the radiochemical transformations in polymers is a vital question for the elaboration of accelerated methods simulating natural conditions to define the radiation resistance of polymers.

**References**

- [1] Barkhudaryan VG. *Polymer* 2000;41:575.
- [2] Charlesby A. *Atomic radiation and polymers*, London: Pergamon, 1960 chap. 13.
- [3] Minkova L, Lefterova E, Koleva Ts. *Polym Degrad Stab* 1992;37(3):247.
- [4] O'Donnel JH, Winzor KL, Winzor DS. *Macromolecules* 1990;23(1):167.
- [5] Crouther JA, Johnson JF, Tanaka J. *Am Chem Soc Polym Prepr* 1978;19(2):840.
- [6] Dakin VI. *Visokomolek Soedin A* 1981;23(2):342.
- [7] France C, Hendra PJ, Maddams WF, Willis HA. *Polymer* 1987;28(5):710.
- [8] Luongo JP. *Polym Lett* 1963;1:141.
- [9] Domareva NM, Kogan SU, Tumarkin NJ. *Visokomolek Soedin A* 1988;30(2):384.
- [10] Zamotaev PV. *Plast Massy* 1984(11):10.
- [11] Patrick E, Cassidy, Tejraj M Aminabhavi. *J Macromol Sci-Rev Macromol Chem C* 1981;21(1):89.
- [12] Klein PG, Brereton MG, Rasburn J, Ward IM. *Macromol Chem Macromol Symp* 1989;30:45.
- [13] Pakhareno VA, Nesolevich IN, Romanova ZA, Kirienko EM. *Plast Massy* 1980(5):20.
- [14] Gorelik BA, Ivanov AI, Semenenko EI, Goldberg VM. *Visokomolek Soedin A* 1978;2(5):987.
- [15] Pletanov VP, Berljangt SM. *Visokomolek Soedin A* 1977;19(8):1679.
- [16] Bykov EV, Bystritskaja EB, Karpukhin ON. *Visokomolek Soedin A* 1987;29(7):1347.
- [17] Arakava Kazuo, Seyuchi Tadao. *Kobuncy Rombunju* 1984;41(12):733.
- [18] Burow SD. *Am Chem Soc Polym* 1964;5:396 preprints.
- [19] Atkhison GA. *J Polym Sci* 1957;35(129):557.
- [20] Bylinitskaja OI, Tykhomirov VS. *Radiatsionnaja khymya polymerov* 1977;2110:42.